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CONTENTS

Physics. — *On the scattering of neutrons in matter.* (V). By L. S. ORNSTEIN. (Communication from the Physical Institute of the University of Utrecht).

(Communicated at the meeting of May 29, 1937.)

In this paper we will discuss the distribution in direction (of the velocity) of neutrons scattered by protons.

In the foregoing papers [1]) we have assumed that the probability of a direction ϑ after one collision of the neutron with a proton is given by the formula

$$2 \sin \vartheta \cos \vartheta \, d\vartheta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ϑ is the direction of velocity for the scattered neutron.

In this paper we will use a more general law — viz. that the original direction of the group of neutrons is an axis of symmetry of the directions of the scattered neutron. We express this law by:

$$W(\vartheta)\, d\vartheta = f(\cos\vartheta) \sin\vartheta \, d\vartheta \; [2]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Integrated with respect to ϑ from 0 to π the result ought to be unity.

Now it is possible to express the frequency law after n collisions by (2) in such a way that we introduce the mean values for $\cos\vartheta$ defined by the relation

$$\overline{\cos \vartheta^p} = \int_0^{\pi} \cos^p \vartheta \, f(\cos\vartheta) \sin\vartheta \, d\vartheta \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As one understands at once that the LEGENDRE polynomia $P_z(\cos\vartheta)$ will play a part, we introduce the mean values of these polynomia by the definition

$$\overline{P_n(\cos\vartheta)} = \overline{P_n(\mu)} = \int_{-1}^{+1} P_n(\mu) f(\mu) \, d\mu \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We now proceed first to the calculation of $\overline{\cos\vartheta_n}$ which represents the mean value of the cosinus after n collisions.

If ϑ_{n-1} is the angle of the direction of the velocity after $n-1$ collisions

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[1]) Cf. These Proceedings **39**, 810, 904, 1049, 1166, (1936).

[2]) In a remark to this paper we will treat the energy distribution when (2) is assumed.

with the original direction and ϑ_n that after n, the last direction is originated from the first by a change of azimuth φ and by turning the direction over an angle ϑ such that:

$$\cos \vartheta_n = \cos \vartheta_{n-1} \cos \vartheta + \sin \vartheta_{n-1} \sin \vartheta \cos \varphi \quad . \quad . \quad . \quad . \quad (5)$$

The probability of this change by a given value of ϑ_{n-1} is given by (2) which must be multiplied by $\frac{d\varphi}{2\pi}$.

In order to get $\overline{\cos \vartheta_n'}$ for a given value of ϑ_{n-1} we must multiply by the probability and integrate over the range of ϑ and with respect to φ from 0 to 2π.

In this way we get for

$$\overline{\cos \vartheta_n'} = \cos \vartheta_{n-1} \overline{\cos \vartheta}$$

or taking the mean with respect to ϑ_{n-1}

$$\overline{\cos \vartheta_n} = \overline{\cos \vartheta_{n-1}} \; \overline{\cos \vartheta}$$

from which follows

$$\overline{\cos \vartheta_n} = \overline{\cos \vartheta}^n = \overline{P_1 (\vartheta)}^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6^1)$$

In the same way we get for $\overline{\cos^2 \vartheta_n}$

$$\begin{aligned} \overline{\cos^2 \vartheta_n} &= \overline{\cos^2 \vartheta_{n-1}} \; \overline{\cos^2 \vartheta} + \overline{\sin^2 \vartheta_{n-1}} \; \overline{\sin^2 \vartheta} \, \tfrac{1}{2} \\ &= \overline{\cos^2 \vartheta_{n-1}} \, \tfrac{1}{2} \{3 \, \overline{\cos^2 \vartheta} - 1\} + \tfrac{1}{2} (1 - \overline{\cos^2 \vartheta}) \end{aligned}$$

from which we can deduce, introducing $\overline{P_2 (\cos \vartheta)}$:

$$\overline{\cos^2 \vartheta_n} = \tfrac{1}{3} (1 + 2 \, \overline{P_2 (\cos \vartheta)}^n) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6^2)$$

and for

$$\overline{\cos^3 \vartheta_n} = \tfrac{2}{5} \, \overline{P_3 (\cos \vartheta)}^n + \tfrac{3}{5} \, \overline{P_1 (\cos \vartheta)}^n \quad . \quad . \quad . \quad . \quad . \quad (6^3)$$

$$\overline{\cos^4 \vartheta_n} = \tfrac{1}{5} (1 + \tfrac{8}{7} \, \overline{P_4 (\cos \vartheta)}^n + \tfrac{2 \cdot 9}{7} \, \overline{P_2 (\cos \vartheta)}^n) \quad . \quad . \quad . \quad (6^4)$$

The generalization of these formulae can be found, if we take into consideration that they originate from the development of $\cos \vartheta$, $\cos^2 \vartheta$, etc. in LEGENDRE polynomia and replacing the first power of $P_n (\vartheta)$ by the nth power of its mean value.

In this way we get, taking into consideration that

$$\left.\begin{aligned} \cos^{2p} \vartheta &= \sum_0^p a_{2k} \, P_{2k} (\cos \vartheta) \\ {}_p a_{2k} &= \frac{4k+1}{2} \int_{-1}^{+1} \mu^{2p} \, P_{2k} (\mu) \, d\mu \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7^1)$$

and

$$\left.\begin{aligned} \cos^{2p+1}\vartheta &= \sum_0^p a_{2k+1}\, P_{2k+1}(\cos\vartheta) \\ {}_pa_{2k+1} &= \frac{4k+3}{2}\int_{-1}^{+1}\mu^{2p+1}\, P_{2k+1}(\mu)\, d\mu \end{aligned}\right\} \quad \ldots\ldots \quad (7^2)$$

$$\overline{\cos^{2p}\vartheta_n} = \sum_0^p {}_pa_{2k}\,\overline{P_{2k}(\cos\vartheta)}^n \quad \ldots\ldots \quad (8^1)$$

and

$$\overline{\cos^{2p+1}\vartheta_n} = \sum_0^p {}_pa_{2k+1}\,\overline{P_{2k+1}(\cos\vartheta)}^n \quad \ldots\ldots \quad (8^2)$$

When n is infinite, the odd mean powers are zero and the even mean powers given by

$$\overline{\cos^{2p}\vartheta} = {}_pa_0 = \tfrac{1}{2}\int_{-1}^{+1}\mu^{2p}\, d\mu = \frac{1}{2p+1}$$

to these values the mean even powers converge for large values of n.

The values mentioned correspond with a homogeneous distribution of the velocities. This distribution is already strongly approximated for rather, not very, great values of n, which means that after a not great number of collisions for any law of scattering the homogeneous distribution results.

If we assume the distribution (1), we get:

$$\overline{\cos^p\vartheta} = \frac{2}{p+2}$$

and we have:

$$\overline{\cos\vartheta_n} = (\tfrac{2}{3})^n$$

$$\overline{\cos^2\vartheta_n} = \tfrac{1}{3}\,(1+2\,(\tfrac{1}{4})^n)$$

$$\overline{\cos^3\vartheta_n} = \tfrac{2}{3\,5}\,(\tfrac{2}{3})^n$$

In the second paper we have shown that the probability of n collisions, when the mean number in which the neutron is not captured is ν_f, p being the probability of capture, is given by:

$$\frac{\nu_f^n\, e^{-\frac{\nu_f}{1-p}}}{n!}.$$

The mean value $\overline{\cos\vartheta_\nu}$ in the case of ν_f collisions free from capture, therefore, is given by:

$$\overline{\cos\vartheta_\nu} = \sum_0^\infty \frac{\nu_f^n\, e^{-\frac{\nu_f}{1-p}}}{n!}\,\overline{\cos\vartheta_n} =$$

$$\sum_0^\infty \frac{\nu_f^n\, e^{-\frac{\nu_f}{1-p}}}{n!}\,\overline{P_1(\vartheta)}^n =$$

$$e^{-\frac{\nu_f}{1-p}}\, e^{\nu_f \overline{P_1(\vartheta)}}$$

From the formula (8^1) and (8^2) we get in the analogous way

$$\left.\begin{aligned} \overline{\cos^{2p}\vartheta_\nu} &= e^{-\frac{\nu_f}{1-p}} \sum_0^p {}_pa_{2k}\, e^{\nu_f \overline{P_{2k}(\cos\vartheta)}} \\ \text{and} \\ \overline{\cos^{2p+1}\vartheta_\nu} &= e^{-\frac{\nu_f}{1-p}} \sum_0^p {}_pa_{2k+1}\, e^{\nu_f \overline{P_{2k+1}(\cos\vartheta)}} \end{aligned}\right\} \quad . \quad . \quad (9)$$

We are now prepared to determine the probability law of ϑ after n collisions, which we denote by $W_n(\vartheta)\sin\vartheta$. We develop this function in an infinite series of LEGENDRE polynomia, so that

$$W_n(\vartheta) = A_0 + A_1 P_1(\cos\vartheta) + \ldots . A_{2p} P_{2p}(\cos\vartheta) + A_{2p+1} P_{2p+1}(\cos\vartheta) \quad (10)$$

Introducing again $\cos\vartheta = \mu$ and integrating $W_n(\mu)\,d\mu$ from -1 to $+1$, we find for $A_0 = \frac{1}{2}$ and, taking into account the condition that the mean values of $\overline{\cos\vartheta^p} = \overline{\mu^p}$ are given by the relation mentioned above, we easily find

$$A_p = \frac{2p+1}{2}\,\overline{P_p(\cos\vartheta)}^n$$

so

$$W_n(\mu) = \sum_0^\infty \frac{2p+1}{2}\,\overline{P_p(\cos\vartheta)}^n\, P_p(\mu) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From this equation we can deduce the value of the frequency law if in the mean ν collisions without capture take place. We get

$$W_\nu(\mu) = e^{-\frac{\nu_f}{1-p}} \sum_0^\infty \frac{2p+1}{2}\, P_p(\mu)\, e^{\nu_f \overline{P_p(\cos\vartheta)}} \quad . \quad . \quad . \quad . \quad (12)$$

The relations (11) and (12) can be used in order to deduce the mean

values af $\cos\vartheta$ for the function which determines the scattering after one collision only from experimental data on the frequency law.

Using the frequency law (1), we find for $W_n(\mu)$,

$$W_n(\mu) = \tfrac{1}{2} + (\tfrac{1}{3})^n \tfrac{3}{2} P_1(\mu) + \sum_1^\infty \frac{4p+1}{2} \left(\frac{(1-)^p\ 2p!}{2^{2p}(p!)^2} \frac{1}{(p+2)(p-1)} \right)^n P_{2p}(\mu)$$

which for large values of n converges to a spherical distribution.

We will conclude this article with some remarks on paper (I).

In this first paper the law of distribution in energy for neutrons scattered by protons has been deduced, assuming that the probability of scattering under a certain angle is given by (1). It is possible to obtain this law under the much more general assumption (2).

Let us first deduce the mean values given at p. 811 of paper I.

The energy after n collisions is given by

$$\varepsilon = \varepsilon_0 \cos^2\vartheta_1 \cos^2\vartheta_2 \ldots . \cos^2\vartheta_n$$

where $\vartheta_1 \ldots \vartheta_n$ are the angles occurring at the successive collisions. Now for each collision the probability is given by (2) so that we get:

$$\overline{\varepsilon_n} = \varepsilon_0\ \overline{\cos^2\vartheta}^n$$

and in general

$$\overline{\varepsilon_n^p} = \varepsilon_0^p\ \overline{\cos^{2p}\vartheta}^n .$$

When we go back to the formula (4) we get the relation given in paper (I).

For the mean p^{th} poder, when the mean number of collisions is ν, we find

$$\overline{\varepsilon^p}^\nu = \varepsilon_0^p\ e^{-\nu}\ e^{\overline{\cos 2p\vartheta}^\nu (1-p)}.$$

We can deduce the probability of an energy between ε and $\varepsilon + d\varepsilon$ after a given number of collisions.

Let us take, for example,

$$W_2(\varepsilon).$$

This probability for the angles ϑ_1 and ϑ_2 is

$$W_2(\varepsilon)\, d\varepsilon = f(\vartheta_1) \sin\vartheta_1\, d\vartheta_1\, f(\vartheta_2) \sin\vartheta_2\, d\vartheta_2,$$

or putting us $\vartheta = \mu$

$$f(\mu_1)\, d\mu_1\ \ f(\mu_2)\, d\mu_2$$

which must be integrated with the conditions

$$\varepsilon < \varepsilon_0 \mu_1^2 \mu_2^2 < \varepsilon + d\varepsilon$$

and

$$\sqrt{\frac{\varepsilon}{\varepsilon_0}} \leqq \mu_1 \leqq 1$$

thus

$$W_2(\varepsilon)\, d\varepsilon = \frac{1}{2\sqrt{\varepsilon \varepsilon_0}} \int_{\sqrt{\frac{\varepsilon}{\varepsilon_0}}}^{1} f(\mu_1)\, f\left(\frac{1}{\mu_1}\sqrt{\frac{\varepsilon}{\varepsilon_0}}\right) \frac{d\mu_1}{\mu_1}\, d\varepsilon.$$

Taking for $f(\mu_1)$ $2\mu_1$ we get back the result obtained in (I).
More generally we obtain the recurrent equation

$$W_n(\varepsilon) = \frac{1}{2\sqrt{\varepsilon}} \int_{\varepsilon}^{\varepsilon_0} W_{n-1}(\varepsilon')\, f\left(\sqrt{\frac{\varepsilon}{\varepsilon'}}\right) \frac{d\varepsilon'}{\sqrt{\varepsilon'}}$$

which for the probability (1) changes into (1) paper I.

In the first paper we have indicated that the energy after one collision for particles showing a direction ϑ with the original directions for neutrons (mass m) with particles of the mass m is

$$\varepsilon_1 = \varepsilon_0 \left(1 - \frac{4\,M\,m}{(M+m)^2} \sin^2 \vartheta\right) =$$

$$\varepsilon_0 \left(\left(\frac{M-m}{M+m}\right)^2 + \frac{4\,m\,M}{(M+m)^2} \cos^2 \vartheta\right) =$$

$$\varepsilon_0 (\alpha + \beta \cos^2 \vartheta).$$

Assuming the probability law (1) we obtain

$$\bar{\varepsilon}_1 = \varepsilon_0 \frac{M^2 + m^2}{(M+m)^2}$$

and

$$\bar{\varepsilon}_n = \varepsilon_0 \left(\frac{M^2 + m^2}{(M+m)^2}\right)^n.$$

For $\overline{\varepsilon_1^p}$ we can easily indicate the value, taking into account that $\overline{\cos^{2p} \vartheta} = \frac{1}{2p+2}$. Using the frequency law (2) we get

$$\bar{\varepsilon}_n = \varepsilon_0 (\alpha + \beta\, \overline{\cos^2 \vartheta})^n$$

where $\overline{\cos^2 \vartheta}$ has to be determined with the use of (2) higher mean values can be determined in analogeous way.

For the frequency law of ε after one collision $W_1(\varepsilon)\, d\varepsilon$ we get (using (1))

$$d\varepsilon\, W_1(\varepsilon) = \frac{d\varepsilon}{\beta\, \varepsilon_0}$$

the range of possible values for ε extending from $\varepsilon = \varepsilon_0$ to $\varepsilon = a\,\varepsilon_0$.

If we want to deduce the frequency law for two collisions $W_2(\varepsilon)$ we ought to consider two cases, e.g. $\varepsilon > a\,\varepsilon_0$ and $a\,\varepsilon_0 > \varepsilon > a^2\,\varepsilon_0$.

We thus find for $W_2(\varepsilon)$

$\varepsilon_0 > \varepsilon > a\,\varepsilon_0$

$$W_2(\varepsilon) = \frac{1}{\beta^2\, \varepsilon_0} \int_{\varepsilon}^{\varepsilon_0} \frac{d\varepsilon}{\varepsilon} = \frac{1}{\beta^2\, \varepsilon_0}\, lg\, \frac{\varepsilon_0}{\varepsilon}$$

$a\,\varepsilon_0 > \varepsilon > a^2\,\varepsilon_0$

$$W_2'(\varepsilon) = \frac{1}{\beta^2\, \varepsilon_0} \int_{a\,\varepsilon_0}^{\frac{\varepsilon}{a}} \frac{d\varepsilon}{\varepsilon} = \frac{1}{\beta^2\, \varepsilon_0}\, lg\, \frac{\varepsilon}{a^2\, \varepsilon_0}.$$

In the same way the probability of an energy ε after three and more collisions may be calculated.

Mathematics. — *Zur Differentialgeometrie der Gruppe der Berührungstransformationen.* III. *Infinitesimale doppelthomogene Berührungstransformationen und ihre Beziehungen zur Mechanik und Elektrodynamik.* Von J. A. SCHOUTEN.

(Communicated at the meeting of May 29, 1937.)

1. *Einleitung.*

In dieser Mitteilung sollen die infinitesimalen doppelthomogenen Berührungstransformationen und ihre Anwendungen zur Sprache kommen. Inzwischen hat mich Herr Prof. F. ENGEL nach der Veröffentlichung der beiden ersten Mitteilungen dieser Serie [1]) freundlichst darauf aufmerksam gemacht, dass schon Herr F. J. DOHMEN in seiner Greifswalder Dissertation des Jahres 1905 [2]) doppelthomogene Berührungstransformationen

[1]) Zur Differentialgeometrie der Gruppe der Berührungstransformationen, Proceedings Royal Acad. Amsterdam, **40** (1937) S. 100—107, S. 236—245.

[2]) Darstellung der Berührungstransformationen in Konnexkoordinaten.

behandelt hat. Merkwürdigerweise haben weder seine nur in Dissertationsform publizierten Resultate noch die in Bd. III der Transformationsgruppen unter „Kritik einiger neuerer Untersuchungen" versteckten Bemerkungen von LIE, die den Ausgangspunkt der Untersuchung bildeten, irgendwie in der Litteratur nachgewirkt. Es soll daher hier kurz darüber berichtet werden was vor Veröffentlichung dieser Serie bekannt gewesen ist. Bei LIE [1]) findet sich zunächst eine klare Definition der doppelthomogenen *Objekt*transformation. Zur doppelthomogenen *Koordinaten*transformation gelangte er, dem Geiste der damaligen Zeit entsprechend, natürlich nicht. Für die Objekttransformationen gibt er aber genau die n. u. h. Bedingungen an, die m. m. den Bedingungen I (25, 29, 30) entsprechen. Weiter gehen die Erörtungen von LIE, die eigentlich nur eine Kritik eines falschen Ansatzes von LINDEMANN darstellen, nicht. Bei DOHMEN werden die vier Koeffizienten a, b, c, d (I S. 103), die bei LIE von vornherein die Werte 1, 0, 0, 1 hatten (dieselben Werte die sich bei mir aus der Forderung der Vertauschbarkeit mit der Gruppe $\mathfrak{F}$ ergeben, eine Forderung die nur bei Betrachtung der Koordinatentransformationen aufkommen kann) frei gelassen und er gelangt zum Uebergang von gewöhnlichen zu doppelthomogenen Berührungstransformationen und umgekehrt. Statt von (I 14, 15) geht er aus von Gleichungen, die den Koordinatengleichungen

$$p_{\varkappa'}\, dx^{\varkappa'} = L\, p_\varkappa\, dx^\varkappa + M\, x^\lambda\, dp_\lambda$$
$$x^{\lambda'}\, dp_{\lambda'} = N\, x^\lambda\, dp_\lambda + P\, p_\varkappa\, dx^\varkappa$$

entsprechen.

Seinem Ansatze entsprechend schaltet er von vornherein die Bedingung $p_\varkappa\, x^\varkappa = 0$ aus und findet die Transformationen dementsprechend in der Form, die nicht von dieser zusätzlichen Bedingung Gebrauch macht. Der Hauptsatz (II S. 242), der gestattet jede beliebige doppelthomogene Berührungstransformationen mit Hilfe von $q+1$ in $x^\varkappa, x^{\varkappa'}$ homogenen Funktionen der Grade $+1, -1$ darzustellen, findet sich bei ihm noch nicht. Dagegen ist ihm die Herleitung einer infinitesimalen doppelthomogenen Berührungstransformation aus einer charakteristischen Funktion bekannt, sowie auch die Beziehung zwischen dieser Funktion und der charakteristischen Funktion der entsprechenden gewöhnlichen Berührungstransformation.

2. *Infinitesimale doppelthomogene Berührungstransformationen.*

Die allgemeinste infinitesimale Berührungstransformation in ξ^h, ζ_a; $h, i, j = 1, \ldots, n$; $a, b, c = 2, \ldots, n$ hat nach LIE [2]) die Form

$$\boxed{\frac{d\xi^1}{d\tau} = \zeta_a \frac{\partial W}{\partial \zeta_a} - W;\ \frac{d\xi^a}{d\tau} = \frac{\partial W}{\partial \zeta_a};\ \frac{\partial \zeta_b}{d\tau} = -\frac{\partial W}{\partial \xi^b} - \zeta_b \frac{\partial W}{\partial \xi^1}} \quad . \quad (1)$$

[1]) Transformationsgruppen, Bd. III, S. 530.

[2]) Transformationsgruppen II, S. 252.

Sie transformiert die Differentialform $d_1\xi^1 - \zeta_a\, d_1\xi^a$ folgendermassen [1])

$$\frac{d}{d\tau}(d_1\xi^1 - \zeta_a\, d_1\xi^a) = -\frac{\partial W}{\partial \xi^1}(d_1\xi^1 - \zeta_a\, d_1\xi^a) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Gehen wir zu den Variabelen η_i über vermöge der Gleichung

$$1 : -\zeta_2 : \ldots : -\zeta_n = \eta_1 : \eta_2 : \ldots : \eta_n . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

und nehmen wir als zusätzliche Bedingung hinzu dass

$$\frac{d}{d\tau}(\eta_h\, d_1\xi^h) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

sein soll, so ergibt sich eindeutig

$$\frac{d\xi^h}{d\tau} = \frac{\partial \mathfrak{V}}{\partial \eta_h};\ \frac{d\eta_i}{d\tau} = -\frac{\partial \mathfrak{V}}{\partial \xi^i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

wo

$$\mathfrak{V} = -\eta_1\, W\left(\xi^h, \frac{-\eta_a}{\eta_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

ist. Die allgemeinste infinitesimale homogene Berührungstransformation hat also die Form (5), wo $\mathfrak{V}$ ein beliebige Funktion von ξ^h, η_i, homogen ersten Grades in η_i ist. (LIE a.a.O. S. 263).

Wir gehen jetzt zu den Variablen x^α, p_α über vermöge

$$\left.\begin{aligned} 1 : \xi^1 : \ldots : \xi^n &= x^0 : x^1 : \ldots : x^n \\ -\eta_j\, \xi^j : \eta_1 : \ldots : \eta_n &= p_0 : p_1 : \ldots : p_n \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

und setzen zunächst mal

$$\left.\begin{aligned} x^0 &= 1;\ x^h = \xi^h \\ p_0 &= -\eta_j\, \xi^j;\ p_i = \eta_i \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Setzen wir dann

$$\mathfrak{T}(x^\varkappa, p_\lambda) = -x^0\, p_1\, W\left(\frac{x^h}{x^0}, \frac{-p_a}{p_1}\right) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so ist $\mathfrak{T}$ homogen ersten Grades sowohl in $x^\varkappa$ als in p_λ und enthält p_0 nicht, sodass

$$\left.\begin{aligned} \frac{dx^h}{d\tau} &= \frac{\partial \mathfrak{T}}{\partial p_h};\ \frac{dx^0}{d\tau} = \frac{\partial \mathfrak{T}}{\partial p_0} \\ \frac{dp_i}{d\tau} = -\frac{\partial \mathfrak{T}}{\partial x^i};\ \frac{dp_0}{d\tau} &= -p_i \frac{\partial \mathfrak{T}}{\partial p_i} + x^h \frac{\partial \mathfrak{T}}{\partial x^h} \\ &= -\mathfrak{T} + p_0 \frac{\partial \mathfrak{T}}{\partial p_0} + \mathfrak{T} - x^0 \frac{\partial \mathfrak{T}}{\partial x^0} \\ &= -\frac{\partial \mathfrak{T}}{\partial x^0} \end{aligned}\right\} \quad . \quad . \quad (10)$$

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[1]) Wir schreiben d_1 zur Unterscheidung von dem Symbol d.

ist. Da

$$\left.\begin{aligned} \frac{d}{d\tau}(p_\varkappa x^\varkappa) &= p_\varkappa \frac{\partial \mathfrak{T}}{\partial p_\varkappa} - x^\varkappa \frac{\partial \mathfrak{T}}{\partial x^\varkappa} = 0, \\ \frac{d}{d\tau}(p_\varkappa \underset{1}{d} x^\varkappa) &= \frac{dp_\varkappa}{d\tau} \underset{1}{d} x^\varkappa + p_\varkappa \underset{1}{d} \frac{dx^\varkappa}{d\tau} = -\frac{\partial \mathfrak{T}}{\partial x^\varkappa} \underset{1}{d} x^\varkappa + p_\varkappa \underset{1}{d} \frac{\partial \mathfrak{T}}{\partial p_\varkappa} \\ &= -\underset{1}{d}\mathfrak{T} + \underset{1}{d}\mathfrak{T} = 0 \end{aligned}\right\} \quad . \quad (11)$$

ist, ist die Differentialform $p_\varkappa \underset{1}{d} x'$ invariant und zwar *unabhängig von der Gleichung* $p_\varkappa x^\varkappa = 0$.

Wir gehen jetzt zu beliebigen homogenen Koordinaten über

$$'x^\varkappa = \varkappa x^\varkappa ; \; 'p_\lambda = \lambda p_\lambda \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

wo die Koeffizienten $\varkappa$ und λ beliebige homogene Funktionen nullten Grades in $x^\varkappa$ und p_λ sind. Sodann ist

$$\frac{d'x^\varkappa}{d\tau} = \frac{d \log \varkappa}{d\tau} {}'x^\varkappa + \varkappa \frac{\partial \mathfrak{T}}{\partial p_\varkappa} ; \; \frac{d'p_\lambda}{d\tau} = \frac{d \log \lambda}{d\tau} {}'p_\lambda - \lambda \frac{\partial \mathfrak{T}}{\partial x^\lambda} \quad . \quad . \quad (13)$$

Wir können aber diese infinitesimale Transformation ändern ohne die geometrische Bedeutung zu ändern, indem wir rechts einen Term $\alpha\, 'x^\varkappa$ bzw. $\beta\, 'p_\lambda$ zufügen. (Denn die Transformation von $\frac{'x^\varkappa}{'x_0}$ und $\frac{'p_\lambda}{'p_0}$ ändert sich dabei nicht). Diese Zusatzterme wollen wir so wählen, dass wiederum sowohl $'p_\varkappa\, 'x^\varkappa$ als $'p_\varkappa \underset{1}{d}\, 'x^\varkappa$ invariant sind, unabhängig von der Gleichung $'p_\varkappa\, 'x^\varkappa = 0$. In anbetracht der Homogenität von $\mathfrak{T}$ können wir schreiben

$$\left.\begin{aligned} \frac{d'x^\varkappa}{d\tau} &= \frac{d \log \varkappa}{d\tau} {}'x^\varkappa + \frac{\partial \mathfrak{T}('x^\varkappa, 'p_\lambda)}{\partial\, 'p_\varkappa} + \alpha\, 'x^\varkappa \\ \frac{d'p_\lambda}{d\tau} &= \frac{d \log \lambda}{d\tau} {}'p_\lambda - \frac{\partial \mathfrak{T}('x^\varkappa, 'p_\lambda)}{\partial\, 'x^\lambda} + \beta\, 'p_\lambda \end{aligned}\right\} \quad . \; . \; . \quad (14)$$

Da

$$\left.\begin{aligned} \frac{d}{d\tau}('p_\varkappa\, 'x') &= \frac{d \log \varkappa}{d\tau} {}'x'\, 'p_\varkappa + \alpha\, 'x'\, 'p_\varkappa \\ &+ \frac{d \log \lambda}{d\tau} {}'x^\varkappa\, 'p_\varkappa + \beta\, 'x^\varkappa\, 'p_\varkappa \end{aligned}\right\} \quad . \; . \; . \quad (15)$$

und

$$\left.\begin{aligned}\frac{d}{d\tau}('p_\varkappa \overset{d}{_1} 'x^\varkappa) &= \frac{d\log\lambda}{d\tau}\,'p_\varkappa \overset{d}{_1} 'x^\varkappa - \overset{d}{_1}\,'x^\varkappa \frac{\partial\mathfrak{T}('x^\varkappa,'p_\lambda)}{\partial\,'x^\varkappa} + \beta\,'p_\varkappa \overset{d}{_1}\,'x^\varkappa \\ &+ 'p_\varkappa \overset{d}{_1}\left(\frac{d\log\varkappa}{d\tau}\,'x^\varkappa + \frac{\partial\mathfrak{T}('x^\varkappa,'p_\lambda)}{\partial\,'p_\varkappa} + \alpha\,'x^\varkappa\right) \\ &= \left(\frac{d\log\lambda}{d\tau}+\beta\right)'p_\varkappa \overset{d}{_1}\,'x^\varkappa + \\ &- \left(\frac{d\log\varkappa}{d\tau}+\alpha\right)'x^\varkappa \overset{d}{_1}\,'p_\varkappa + \overset{d}{_1}\left\{\left(\frac{d\log\varkappa}{d\tau}+\alpha\right)'x^\varkappa\,'p_\varkappa\right\}\end{aligned}\right\}. \quad (16)$$

ist, werden diese beiden Ausdrücke unabhängig von der Gleichung $p_\varkappa x^\varkappa = 0$ und für jedes Differential $\overset{d}{_1}$ Null wenn

$$\alpha = -\frac{d\log\varkappa}{d\tau}; \quad \beta = -\frac{d\log\lambda}{d\tau} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

ist, sodass die gewünschte infinitesimale Transformation lautet

$$\left.\begin{aligned}\frac{d\,'x^\varkappa}{d\tau} &= \frac{\partial}{\partial\,'p_\varkappa}\mathfrak{T}('x^\varkappa,'p_\lambda) \\ \frac{d\,'p_\lambda}{d\tau} &= -\frac{\partial}{d\,'x^\lambda}\mathfrak{T}('x^\varkappa,'p_\lambda)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Die Funktion $\mathfrak{T}$ enthält p_0 nicht. Bilden wir nun aber eine beliebige Funktion, die sich vermöge $'p_\lambda\,'x^\lambda = 0$ in $\mathfrak{T}$ überführen lässst, also

$$'\mathfrak{T}('x^\varkappa,'p_\lambda) = \mathfrak{T}('x^\varkappa,'p_\lambda) + ('p_\lambda\,'x^\lambda)\,F('x^\varkappa,'p_\lambda), \quad . \quad . \quad . \quad (19)$$

so stellt

$$\left.\begin{aligned}\frac{d\,'x^\varkappa}{d\tau} &= \frac{\partial\,'\mathfrak{T}}{\partial\,'p_\varkappa} = \frac{\partial\mathfrak{T}}{\partial\,'p_\varkappa} + 'x^\varkappa F + ('p_\lambda\,'x^\lambda)\frac{\partial F}{\partial\,'p_\varkappa} \\ \frac{d\,'p_\lambda}{d\tau} &= -\frac{\partial\,'\mathfrak{T}}{\partial\,'x^\lambda} = -\frac{\partial\mathfrak{T}}{\partial\,'x^\lambda} - 'p_\lambda F - ('p_\lambda\,'x^\lambda)\frac{\partial F}{\partial\,'x^\lambda}\end{aligned}\right\} \quad . \quad . \quad (20)$$

eine infinitesimale Transformation dar, die infolge $'p_\lambda\,'x^\lambda = 0$ dieselbe geometrische Bedeutung hat als (18). Da sich mit Hilfe von $'p_\varkappa\,'x^\varkappa = 0$ aus jeder beliebigen homogenen Funktion ersten Grades in $'x^\varkappa$ und $'p_\lambda$ in dieser Weise eine ebensolche Funktion herstellen lässt, die p_0 nicht enthält, haben wir also den Satz erhalten:

Hauptsatz.

Die allgemeinste infinitesimale doppelthomogene Berührungstransformation hat die Form

$$\frac{dx^\varkappa}{d\tau} = \frac{\partial\mathfrak{T}}{\partial p_\varkappa}; \quad \frac{dp_\lambda}{d\tau} = -\frac{\partial\mathfrak{T}}{\partial x^\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

wo $\mathfrak{T}$ *eine beliebige homogene Funktion ersten Grades in* $x^\varkappa$ *und* p_λ *darstellt.*

Ausserdem haben wir den Weg gefunden der von der Funktion $W(\xi^h, \zeta_a)$ zur Funktion $\mathfrak{T}$ führt, es darf für $\mathfrak{T}$ eben jede in $x^\varkappa$ und p_λ homogene Funktion ersten Grades genommen werden, die sich vermöge $p_\varkappa x^\varkappa = 0$ in

$$-x^0 p_1 W\left(\frac{x^h}{x^0}, \frac{-p_a}{p_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

überführen lässt [1]).

3. *Symmetrisierung eines mechanischen Problems i. b. auf t.* [2])

Es sei ein mechanisches (oder elektrodynamisches) Problem vorgelegt in den Koordinaten ξ^p; $p, q, r = 1, \ldots, n-1$ mit einer LAGRANGEfunktion L, die von ξ^p, $\dot{\xi}^p$ und t abhängt und nicht identisch verschwindet. Die Bewegungsgleichungen lassen sich sowohl in der LAGRANGEschen Form

$$\frac{d}{dt}\frac{\partial}{\partial \dot{\xi}^q} L - \frac{\partial L}{\partial \xi^q} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

als in der HAMILTONschen Form

$$\left.\begin{aligned} \partial^p H = \dot{\xi}^p\,;\ \partial_q H = -\dot{\zeta}_p\,;\ \partial^p = \frac{\partial}{\partial \zeta_p}\,;\ \partial_q = \frac{\partial}{\partial \xi^q} \\ H = \zeta_p \dot{\xi}^p - L\,;\ \zeta_q = \frac{\partial L}{\partial \dot{\xi}^q} \end{aligned}\right\} \quad . \quad . \quad (24)$$

schreiben.

Wir schreiben jetzt $t = \xi^n, H = -\zeta_n$ und führen eine neue infinitesimale Grösse $d\tau$ ein um den Gebrauch von Differentialen zu vermeiden [3]). Es sei dann

$$\mathfrak{L} = -H\frac{dt}{d\tau} + \zeta_p \dot{\xi}^p \frac{dt}{d\tau} = \zeta_a \dot{\xi}^a \frac{dt}{d\tau}\,;\ a, b, c = 1, \ldots, n \quad . \quad (25)$$

sodass

$$\mathfrak{L}\, d\tau = L\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

ist und es sei

$$\mathfrak{H}(\zeta_a, \xi^a) = \frac{dt}{d\tau}(-L + \zeta_p \dot{\xi}^p + \zeta_n) = -\mathfrak{L} + \zeta_a \frac{d\xi^a}{d\tau} \quad . \quad . \quad . \quad (27)$$

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[1]) F. J. DOHMEN, a. a. O. S. 40.

[2]) In der Arbeit Homogeneous variables in classical dynamics von P. A. M. DIRAC (Proc. Cambr. Phil. Soc. **29** (1933) 389—400) tritt diese Symmetrisierung auf als erste Homogenisierung, bei welcher die LAGRANGEsche Funktion homogen ersten Grades in den Geschwindigkeiten wird. Da die Kontakttransformation hier aber noch nicht homogen gemacht wird, ziehen wir den Ausdruck Symmetrisierung vor.

[3]) Man kann $d\tau$ dem Probleme irgendwie angepasst wählen aber auch ohne Einführung von $d\tau$ rein mit den Differentialen arbeiten.

$\mathfrak{L}$ ist die neue LAGRANGEsche Funktion homogen erster Ordnung in den Geschwindigkeiten, und man arbeitet mit der HAMILTONschen Gleichung $\mathfrak{H} = 0$ anstatt mit einer HAMILTONschen Funktion.

Die Bewegungsgleichungen lauten jetzt, wie man leicht verifiziert, in der LAGRANGEschen Form

$$\frac{d}{d\tau}\frac{\partial \mathfrak{L}}{\partial \dot{\xi}^b} - \frac{\partial \mathfrak{L}}{\partial \xi^b} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

wo jetzt der Punkt Differentiation nach τ darstellt. $\mathfrak{L}$ ist als Funktion der ξ^a und $\frac{d\xi^a}{d\tau}$ homogen ersten Grades in den „Geschwindigkeiten" $\dot{\xi}^b$. In der HAMILTONschen Form lauten die Gleichungen

$$\partial^a \mathfrak{H} = \frac{d\xi^a}{d\tau}\,;\ \partial_b \mathfrak{H} = -\frac{d\zeta_b}{d\tau}\,;\ \partial_b = \frac{\partial}{\partial \xi^b}\,;\ \partial^a = \frac{\partial}{\partial \zeta^a} \quad . \quad . \quad . \quad (29)$$

Die Funktion $\mathfrak{H}$ ist nicht die einzige Funktion, die den HAMILTONschen Gleichungen genügt. Ist $\mathfrak{T}(\mathfrak{H})$ eine Funktion von $\mathfrak{H}$, die für $\mathfrak{H} = 0$ verschwindet, so ist

$$\partial^a \mathfrak{F} = \frac{\partial \mathfrak{F}}{\partial \mathfrak{H}}\frac{d\xi^a}{d\tau}\,;\ \partial_b \mathfrak{F} = -\frac{\partial \mathfrak{F}}{\partial \mathfrak{H}}\frac{\partial \zeta_b}{d\tau} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

und die Gleichung $\mathfrak{F} = 0$ ist also ebenfalls als HAMILTONsche Gleichung zu verwenden, wenn man $d\tau$ ersetzt durch $d\tau' = d\tau \Big/ \frac{\partial \mathfrak{F}}{\partial \mathfrak{H}}$.

4. *Die erste Homogenisierung.* [1]).

Die Gleichungen (29) stellen eine infinitesimale Kontakttransformation in den Variabelen $\xi^{n+1}, \xi^a, \zeta_a$ dar, vorausgesetzt, dass man sie erzängt durch eine Gleichung für ξ^{n+1} von der Form

$$\frac{d\xi^{n+1}}{d\tau} = \zeta_a \partial^a \mathfrak{H} - \mathfrak{H}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Sie haben die besondere Eigenschaft, dass $\mathfrak{H}$ nicht von ξ^{n+1} abhängt. Infolgedessen ist $\underset{1}{d}\,\xi^{n+1} - \zeta_a \underset{1}{d}\,\xi^a$ invariant:

$$\left.\begin{aligned} \underset{1}{d}(\underset{1}{d}\xi^{n+1} - \zeta_a \underset{1}{d}\xi^a) &= \underset{1}{d}\,\underset{1}{d}\xi^{n+1} - \underset{1}{d}\zeta_a \underset{1}{d}\xi^a - \zeta_a \underset{1}{d}\,\underset{1}{d}\xi^a \\ &= \{\underset{1}{d}(\zeta_a \partial^a \mathfrak{H} - \mathfrak{H}) + (\underset{1}{d}\xi^a)\partial_a \mathfrak{H} - \zeta_a \underset{1}{d}\partial^a \mathfrak{H}\}\, d\tau \\ = \{(\underset{1}{d}\zeta_a)\partial^a \mathfrak{H} - \underset{1}{d}\mathfrak{H} + (\underset{1}{d}\xi^a)\partial_a \mathfrak{H} &+ \zeta_a \underset{1}{d}\partial^a \mathfrak{H} - \zeta_a \underset{1}{d}\partial^a \mathfrak{H}\}\, d\tau = 0. \end{aligned}\right\} \quad . \quad . \quad (32)$$

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[1]) Diese erste Homogenisierung tritt bei DIRAC a. a. O. auf als zweite Homogenisierung, nämlich Homogenisierung der Momente.

Aus (31) folgt

$$\frac{d\xi^{n+1}}{d\tau} = \zeta_a \frac{d\xi^a}{d\tau} - \mathfrak{H} = \mathfrak{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

und das Differential $d\xi^{n+1}$ der Hilfsvariablen ξ^{n+1} hat also die Bedeutung von $\mathfrak{L}\,d\tau = L\,dt$. Wir gehen jetzt zu den homogenen Momenten η_i; $h, i = 1, \ldots, n+1$ über und definieren

$$\zeta_a = -\frac{\eta_a}{\eta_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Dann geht aus (33) hervor

$$\mathfrak{H} = -\frac{\eta_a}{\eta_{n+1}}\,\dot{\xi}^a - \mathfrak{L} = -\frac{\eta_h}{\eta_{n+1}}\,\dot{\xi}^h \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Führen wir jetzt statt $\mathfrak{H}$ die Funktion

$$\mathrm{H} = -\eta_{n+1}\,\mathfrak{H}\left(\xi^h, \frac{-\eta_a}{\eta_{n+1}}\right) = \eta_h\,\dot{\xi}^h \quad . \quad . \quad . \quad . \quad . \quad (36)$$

ein, homogen ersten Grades in η_i, so ist (vgl. 5)

$$\boxed{\frac{\partial \mathrm{H}}{\partial \eta_h} = \dot{\xi}^h \quad ; \quad \frac{\partial \mathrm{H}}{\partial \xi^i} = -\dot{\eta}_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

und dies sind die Bewegungsgleichungen in der HAMILTONschen Form nach der ersten Homogenisierung. Sie stellen eine homogene infinitesimale Kontakttransformation dar. Zu Ihnen gesellt sich die Gleichung

$$\boxed{\mathrm{H} = 0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Auch hier gelingt es die Gleichungen in der LAGRANGEschen Form zu schreiben [1]).

5. *Die zweite Homogenisierung.*

Wir gehen jetzt zu den Koordinaten x^i und den Momenten p_i über definiert durch

$$\left.\begin{aligned} x^0 : x^1 : \ldots : x^{n+1} &= 1 : \xi^1 : \ldots : \xi^{n+1} \\ p_0 : p_1 : \ldots : p_{n+1} &= -\eta_l\,\xi^i : \eta_1 : \ldots : \eta_{n+1} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (39)$$

und führen statt $\mathfrak{H}$ die Funktion

$$\mathbf{H} = -x^0\,p_{n+1}\,\mathfrak{H}\left(\frac{x^h}{x^0}; \frac{-p_a}{p_{n+1}}\right) \quad . \quad . \quad . \quad . \quad . \quad (40)$$

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[1]) DIRAC a. a. O. S. 394.

ein, homogen ersten Grades in $x^\varkappa$ und in p_λ. Sodann ist (vgl. 10)

$$\frac{\partial \mathbf{H}}{\partial p_\varkappa} = \dot{x}^\varkappa ; \quad \frac{\partial \mathbf{H}}{\partial x^\lambda} = -\dot{p}_\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

und dies sind die Bewegungsgleichungen in der HAMILTONschen Form nach der zweiten Homogenisierung. Sie stellen eine doppelthomogene Kontakttransformation dar. Zu Ihnen gesellt sich die Gleichung

$$\mathbf{H} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

und es liessen sich natürlich auch hier Gleichungen in der LAGRANGEschen Form finden.

6. *Die elektrodynamischen Bewegungsgleichungen in der gewöhnlichen allgemeinen Relativitätstheorie.*

Die Symmetrisierung der elektrodynamischen Bewegungsgleichungen führt bekanntlich zu einer Funktion $\mathfrak{H}$ von der Form

$$\mathfrak{H} = \tfrac{1}{2} m c^2 - \frac{1}{2m} g^{hi} \left(\eta_h - \frac{e}{c} \varphi_h \right) \left(\eta_i - \frac{e}{c} \varphi_i \right) \quad . \quad . \quad (43)$$

wenn $d\tau$ gemäss

$$d\tau^2 = g_{hi} \, d\xi^h \, d\xi^i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

gewählt wird (Signatur $- - - +$).

Die erste Homogenisierung führt zu [1])

$$\mathrm{H} = -\tfrac{1}{2} m c^2 \eta_5 + \frac{1}{2m} \eta_5 g^{hi} \left(-\frac{\eta_h}{\eta_5} - \frac{e}{c} \varphi_h \right) \left(-\frac{\eta_i}{\eta_5} - \frac{e}{c} \varphi_i \right) \quad (45)$$

und die zweite zu

$$\mathbf{H} = -\tfrac{1}{2} m c^2 p_5 x_0 + \frac{1}{2m} p_5 x^0 g^{hi} \left(-\frac{p_h}{p_5} - \frac{e}{c} \varphi_h \right) \left(-\frac{p_i}{p_5} - \frac{e}{c} \varphi_i \right). \quad (46)$$

Die Homogenisierungen führen also nicht zu Formen, symmetrisch in ξ^h, η_i bzw. $x^\varkappa, p_\lambda$. Wir wollen nun aber zeigen, dass dies nur an der besonderen Methode liegt, die hier verwendet wird um Homogenisierungen zu erzwingen, und dass sich auf anderem Wege eine vollkommen symmetrische doppelthomogene Darstellung finden lässt.

7. *Die elektrodynamischen Bewegungsgleichungen in der projektiven Feldtheorie.*

In der projektiven Feldtheorie [2]) haben wir von vornherein homogene Koordinaten $x^\varkappa, \varkappa, \ldots, \tau = 0, 1, \ldots, 4$.

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[1]) Vgl. DIRAC a. a. O. S. 400.

[2]) J. A. SCHOUTEN, La théorie projective de la relativité; Annales de l'Institut HENRI POINCARÉ, **5** (1935) 51—88.

Dementsprechend ist der Lokalraum zunächst ein projektiver Raum. Die Metrik wird eingeführt mittels einer Grösse $G_{\lambda\varkappa}$ für welche gilt

$$G_{\lambda\varkappa}\, x^{\lambda}\, x^{\varkappa} = -\chi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

wo $G_{\lambda\varkappa}$ homogen vom Grade -2 in $x^{\varkappa}$ und χ^2 eine positive Konstante ist, die die Dimension $[L^2]$ hat. Die Beziehungen zwischen dem gewöhnlichen Fundamentaltensor g_{ih} und $G_{\lambda\varkappa}$ lauten

$$g_{ih}\frac{\partial \xi^i}{\partial x^{\lambda}}\frac{\partial \xi^h}{\partial x^{\varkappa}} - q_{\lambda}\, q_{\varkappa} = G_{\lambda\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

wo

$$q_{\lambda} = G_{\lambda\varkappa}\, q^{\varkappa} \; ; \; q^{\varkappa} = \chi^{-1}\, x^{\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

ist. Es gibt eine (projektive) Uebertragung, die $G_{\lambda\varkappa}$ invariant lässt und für deren Parameter $\Pi^{\varkappa}_{\mu\lambda}$ gilt

$$\left.\begin{aligned} \Pi^{\varkappa}_{\mu\lambda} &= \left\{ \begin{matrix} \varkappa \\ \mu\ \lambda \end{matrix} \right\} + (q-1)\, q_{\mu\lambda}\, q^{\varkappa} + (1-p)\, q_{\mu}\, q_{\lambda}^{\ \varkappa} + (1-q)\ q_{\lambda}\, q_{\mu}^{\ \varkappa} \\ x^{\mu}\, \Pi^{\varkappa}_{\mu\lambda} &= -\chi\, p\, q^{\varkappa}_{\ .\lambda} - \mathfrak{R}^{\varkappa}_{\lambda}\,; \; q_{\mu\lambda} = \partial_{[\mu} q_{\lambda]} \\ x^{\lambda}\, \Pi^{\varkappa}_{\mu\lambda} &= -\chi\, q\, q^{\varkappa}_{\ .\mu} - \mathfrak{R}^{\varkappa}_{\mu} \end{aligned}\right\} \quad (50)$$

wo das CHRISTOFFEL-symbol $\{\ \}$ sich auf $G_{\lambda\varkappa}$ bezieht, p und q Konstanten sind und $q_{\mu\lambda}$ folgendermassen mit dem Bivektor F_{ji} des elektromagnetischen Feldes zusammenhängt

$$\left.\begin{aligned} q_{\mu\lambda} &= \frac{1}{2}\,\frac{k}{c}\,\frac{\partial \xi^j}{\partial x^{\mu}}\,\frac{\partial \xi^i}{\partial x^{\lambda}}\, F_{ji}\,; \\ k &= \frac{q}{\sqrt{q^2 - 2pq + p}}\sqrt{\frac{\varkappa}{2}}\,; \; \varkappa = \text{Gravitationskonstante} = 1{,}87\,.\,10^{-27}\,[M^{-1}\,L]. \end{aligned}\right\} \quad (51)$$

Der Vektor der Vierergeschwindigkeit ist

$$i^{\varkappa} = \frac{1}{c}\left(\frac{dx^{\varkappa}}{d\tau} + q^{\varkappa}\, q_{\lambda}\,\frac{dx^{\lambda}}{d\tau}\right) = i^{\mu}\,\partial_{\mu}\, x^{\varkappa} \quad . \quad . \quad . \quad . \quad (52)$$

und es ist also $i^{\varkappa}\, q_{\varkappa} = 0$ und $i^{\varkappa}\, i_{\varkappa} = +1$.

Der totale (potentielle + kinetische) Impuls wird dargestellt durch einen Punkt in dem projektiven Lokalraum, den *Impulsenergiepunkt*

$$p^{\varkappa} = m\, c\, i^{\varkappa} + \frac{e}{k}\, q^{\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

Die Forderung, dass die autogeodätischen Linien der Uebertragung, definiert durch

$$p^{\mu}\, \nabla_{\mu}\, p^{\varkappa} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

die Bahnkurven der geladenen Teilchen sind, führt zur Bedingung

$$p + q = 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

und zur Gleichung

$$i^{\mu}\,\partial_{\mu}\,p_{\lambda}=\frac{1}{m\,c}\;\Pi^{\varrho}_{\sigma\lambda}\,p^{\sigma}\,p_{\varrho}+\frac{\varrho}{\chi\,m\,c\,k}\,p_{\lambda} \quad . \quad . \quad . \quad . \quad . \quad (56)$$

Aus (53) folgt

$$\left.\begin{aligned} G^{\lambda\mu}\,p_{\lambda}\,p_{\mu}&=+\,m^2\,c^2-\frac{e^2}{k^2}\\ p_{\lambda}\,q^{\lambda}&=-\,\frac{e}{k}\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

woraus hervorgeht, dass

$$\mathbf{F}(p,q)=\frac{1}{2\,mc}\left\{G^{\varkappa\lambda}\,p_{\varkappa}\,p_{\lambda}-\frac{2e}{\chi k}\,p_{\lambda}\,x^{\lambda}+\chi^{-2}\left(\frac{e^2}{k^2}+m^2c^2\right)G_{\lambda\varkappa}\,x^{\lambda}\,x^{\varkappa}\right\}=0\,. \quad (58)$$

ist. Nun ist unter Berücksichtigung von (53) und $p+q=2$

$$\left.\begin{aligned} \frac{\partial\mathbf{F}}{\partial\,p_{\varkappa}}&=\frac{1}{mc}\left(p^{\varkappa}-\frac{e}{k}\,q^{\varkappa}\right)=i^{\varkappa}=\frac{d'\,x^{\varkappa}}{d\,\tau};\;\frac{d'}{d\,\tau}=i^{\mu}\,\partial_{\mu}\\ \frac{\partial\mathbf{F}}{\partial\,x^{\lambda}}&=\frac{1}{2\,mc}\left(p_{\varrho}\,p_{\sigma}\,\partial_{\lambda}\,G^{\varrho\sigma}-\frac{2e}{\chi k}\,p_{\lambda}\right)\\ &=\frac{1}{mc}\left(-\Pi^{\sigma}_{\varrho\lambda}\,p^{\varrho}\,p_{\sigma}-\frac{e}{\chi k}\,p_{\lambda}\right)=-\,\frac{d'\,p_{\lambda}}{d\,\tau}\end{aligned}\right\} \quad . \quad . \quad (59)$$

sodass sich $\mathbf{F}$ als HAMILTONsche Funktion bewährt. Nur ist $\mathbf{F}$ nicht homogen in p_{λ} und $x^{\varkappa}$. Nun ist aber $p_{\lambda}\,x^{\lambda}=-\,\frac{\chi e}{k}$. Setzt man

$$\mathbf{H}=\frac{1}{2\,mc}\left\{-\frac{\chi e}{k}\,\frac{G^{\varkappa\lambda}\,p_{\varkappa}\,p_{\lambda}}{p_{\varrho}\,x^{\varrho}}-\frac{e}{\chi k}\,p_{\lambda}\,x^{\lambda}+\frac{m^2\,c^2}{\chi^2}\,\frac{k}{e\,\chi}\,G_{\lambda\varkappa}\,x^{\lambda}\,x^{\varkappa}\,p_{\varrho}\,x^{\varrho}\right\}, \quad . \quad (60)$$

so folgt bei Differentiation nach einigen Umrechnungen

$$\frac{\partial\mathbf{H}}{\partial\,p_{\varkappa}}=\frac{d'\,x^{\varkappa}}{d\,\tau};\;\;\frac{\partial\mathbf{H}}{\partial\,x^{\lambda}}=-\,\frac{d'\,p_{\lambda}}{d\,\tau} \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

womit die gewünschte doppelte Homogenisierung mit homogenem $\mathbf{H}$ erreicht ist.

Es ist zu beachten, dass $\mathbf{H}$ nicht verschwindet und statt dessen die aus (58) und (60) folgende Gleichung

$$\mathbf{H}=mc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

gilt.

Chemistry. — *The Exact Measurement of the Specific Heats of Metals at High Temperatures.* **XXVIII.** *The Heat-Capacity and the Electrical Resistance of Didymium between 300° and 600° C.* By F. M. JAEGER, J. A. BOTTEMA and E. ROSENBOHM.

(Communicated at the meeting of May 29, 1937.)

§ 1. In the course of the determination of the heat-capacity curves of *didymium*, the rather sharp melting-point of the latter was found to be 678° C. From the RÖNTGEN-spectrogram the apparent "molecular weight" of *didymium* could, by direct comparison with the dimensions of the elementary cell of pure *praseo-* and *neodymium* [1]), not be estimated with sufficient accuracy so as to establish in this way the exact composition of the mixture of the two metals, because of the too small differences between the parameters of the latter. The mean composition of *didymium*, as given in the literature, is nearly always: 1 at. of *praseodymium* and 2 at. of *neodymium* [2]). As the melting-points of *praseodymium*: 940° C. and of *neodymium*: 840° C. are known, the melting-point curve of the binary system evidently has a *minimum* at or about at 678° C., — this minimum being situated more closely to the side of the lower melting *neodymium*, as beforehand could have been expected. The other possibility: that of the occurrence of an "eutectic" temperature, is most improbable, as the two very similar metals certainly form an *un*interrupted series of mixed crystals. In connection with the fact that the two components themselves have several transition-points, we will afterwards still return to the question as to the exact form of the diagram of this binary system.

§ 2. *The Heat-capacity curves of Didymium.* By means of SALADIN-LE CHATELIER's method, the heat-capacity of *didymium* at different temperatures was compared with that of *copper*. The curve obtained is

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[1]) The β-modifications of both *praseodymium* and *neodymium* are hexagonal with: $a_0 = 3{,}657 \pm 0{,}010$ Å.U., $c_0 = 5{,}924 \pm 0{,}020$ Å.U. and $a_0 = 3{,}657 \pm 0{,}007$ Å.U., $c_0 = 5{,}880 \pm 0{,}020$ Å.U. respectively; the elementary cell contains 2 atoms. The densities of the two metals at 18° C. are 6,770 and 6,984 respectively. Cf.: M. C. NEUBURGER, *Die Allotropie der Chemischen Elemente*, Stuttgart, (1936), 45, 46, where all references about the literature are given. For the *didymium* investigated, Dr. BEINTEMA even found slightly *greater* parameters for the elementary cell: $a_0 = 3{,}683$ Å.U. $\pm 0{,}007$ and $c_0 = 5{,}929$ Å.U. $\pm 0{,}012$. No certain conclusions could, therefore, be drawn from these data. According to F. TROMBE (Compt. rend. Paris, **198**, (1934), 1592) *neodymium* also manifests a magnetic transition-point at —164° C.; for this reason the hexagonal form is here discerned as the β-modification, in agreement with the case of *cerium* and *lanthanum*, and the cubic modification is indicated as the γ-form. Most probably *praseodymium* shows the same sequence of allotropic modifications, as certainly the β- and γ-forms are already actually observed.

[2]) W. MUTHMANN and L. STÜTZEL, Ber. d. d. Chem. Ges., **32**, (1899), 2676.

represented in Fig. 1. From this figure it is seen that between 560° and

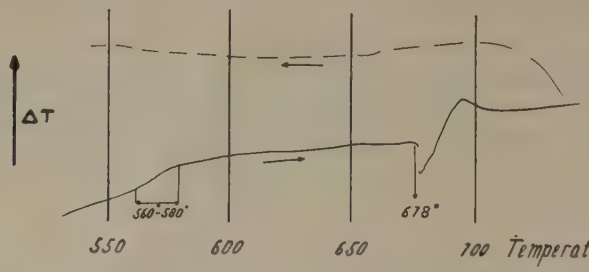

Fig. 1. *Differential heat-capacity curve of Didymium compared with Copper.*

580° C. evidently a new state of the metal (δ) makes its appearance. perhaps corresponding to the analogous transformation $\gamma \leftrightarrows \delta$, which also is observed in the case of pure *neodymium* between 694° and 713° C. The shift of the transition-interval towards lower temperatures here observed is in agreement with the fact that, in the case of the formation of solid solutions, the transition-points of one or both components of a binary system are always changed, — either in positive or negative direction, — by the admixture of the other component and to an extent depending on the momentary concentration of the binary mixture. As we shall see, the field of existence of the mixed crystals in the δ-state is situated above 567° C.

§ 3. These facts are still more clearly illustrated by the study of the change of the *electrical resistance of didymium with the temperature*. For this purpose an *U*-shaped piece of the metal was prepared from a disc cut from a massive lump of the metal at our disposal (99 %*Di*; traces of *iron, magnesium, aluminium* and *silicon*). The terminals of this flat piece of metal had a length of about 50 mm.; the almost quadratic cross-section measured 2 × 2 mm. The two terminals were perforated and two thick *copper* wires of 3 mm. diameter fixed to them by clinching. The apparatus used was the same as previously described in the case of *titanium*. As the resistance of the metal at 20° C. proved to be only 0,00710 Ohm, the change of the resistance of the *copper* wires with the temperature could *not* be neglected in these measurements and had, therefore, afterwards to be determined by separate measurements between 20° and 1000° C. The latter resistances were found to be: 0,01930 Ohm at 100° C.; 0,02106 Ohm at 500° and 0,02344 Ohm at 1000° C. The change of the electrical resistance of *copper* with the temperature proved, therefore, to be perfectly linear. The current in the WHEATSTONE-bridge and the sensitivity of the vertically recording galvanometer were arranged in such a way, that a difference in the resistance of 0,010 Ohm proved to correspond to a deviation of 100 mm. on the photographic plate; thus a variation of 0,0001 Ohm could be measured with perfect certainty and 0,00001 Ohm could be estimated with a fair degree of accuracy, — as was corroborated

by a series of measurements with *copper* between 20° and 1000° C., under repeatedly reversing of the bridge-current. Carefully calibrated resistances of comparison of 0,0200 and of 0,0400 Ohm, made of copper wires of suitable diameters, were used in these experiments as standards. The results obtained in this way are collected in the following table and are graphically represented in Fig. 2.

TABLE I.

Change of the Electrical Resistance of Didymium with the Temperature between 20° and 600° C.

Temperature in ° Cent.:	Resistance in Ohms:	Temperature in ° Cent.:	Resistance in Ohms:
20°	0.00710	500°	0.01007
100	0.00763	508	0.01008*
150	0.00795	520	0.00988 (min.)
200	0.00825	550	0.00982
250	0.00863	577	0.00995
300	0.00894	600	0.01009
350	0.00932		
400	0.00951		
450	0.00981		

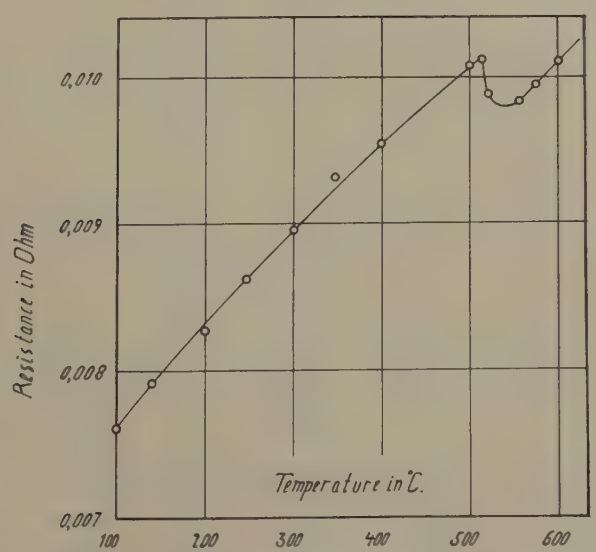

Fig. 2. *The Dependency of the Electrical Resistance of Didymium on the Temperature between 20° and 600° C.*

From these data and Fig. 2 it may be concluded that there is a transmation $\gamma \leftrightarrows \delta$ apparently beginning at about 508° C. and being completed at about 540° C., where a rather deep *minimum* in the curve occurs. The inclination of the curve above 550° C. seems to be about the same as between 400° and 508° C. As we soon shall see from the results of the calorimetrical measurements, the transition truly seems to occur in the interval of 550°—567° C.

§ 4. *The Calorimetrical Measurements.* The determination of the specific heats of *didymium* presented many difficulties, because of the persistent retardation-phenomena manifesting themselves. We only could finally get rid of them after a very great number of heatings at higher temperatures and subsequent coolings and then preserving the sample at ordinary temperatures during several weeks. The metal was enclosed within a platinum vacuum crucible of the usual shape. The data obtained are collected in table II and the graphical representation is given in Fig. 3.

In connection with these data (see Fig. 3) the following remarks can be made: the weight of the massive block of *didymium* was 16,6132 grammes, that of the *platinum* used 28,5355 grammes; the accuracy of the measurements was about 0,2 %. As long as the sample is not completely "stabilized", — which only occurs after *very numerous* heatings and after the metal has subsequently been preserved during several weeks, — the data of $\bar{c}_p$ show *ir*reproducible and strongly scattered values, whilst also the time τ in which the total amount of heat of the sample is given off to the calorimeter-block proves to be variable within wide limits. There can be no doubt about the fact that all the experiments, Nos. 1—56, relate to *non*-stabilized inner conditions of the metal: the dotted curves, — all situated *above* that corresponding to the finally reached *stabilized* state, — *in general* show the trend more and more to approach on subsequent heatings and coolings to the lowest, fully-drawn curve $FBCDE$, exactly as previously was observed with *zirconium* on heating and cooling its single crystals [1]). The complex of scattered points, moreover, clearly allows a subdivision into *three* separate fields, thus beforehand indicating the presence of discontinuities in the vicinity of L, Q and X and of Y at about 435°—440° C. to 470° C. and at 565° C. respectively. Indeed, in the finally reached stable condition of the metal, the said transitions (BC) and D were determined more exactly to occur at 442°—467° (interval) and 567° C. respectively. The scattering of the data concerning the non-stabilized states is most conspicuous in the temperature-intervals $LQXRS$ (430° to 515° C.) and YWE (565° to 590° C.), i.e. immediately after having passed the two transition-temperatures mentioned; moreover, the occurrence of a maximum R in one of the curves relating to those metastable conditions

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[1]) F. M. JAEGER and W. A. VEENSTRA, Rec. d. Trav. d. Chim. d. Pays-Bas, **53**, (1934), 922.

TABLE II.

The mean Specific Heats $\bar{c}_p$ of Didymium between 20° and 600° C.

Sequence-number of the Experiments:	Temperature t in °Cent.:	Final temperature t' of the Calorimeter:	Increase of the temperature $\triangle t$ in μV:	Quantity of Heat Q delivered between $t°$ and t' by 1 Gr. of the substance in Calories:	Quantity of Heat Q_{20} given off between $t°$ and 20° C. by 1 Gr. of the substance in Calories:	Time τ in Minutes, necessary for reaching the maximum Calorimeter temp.:	Mean Specific Heats $\bar{c}_p$ between $t°$ and t' in Calories:
1	323.63	20.96	718.0	17.67	(Here only the values of Q_{20} are mentioned, which are used in the calculation of $\bar{c}_p$).	6	0.05839
2	352.17	20.89	792.3	19.59		6	0.05913
3	382.57	20.89	870.1	21.56		6	0.05961
4	422.4	20.90	970.1	24.04		6	0.05986
5	454.06	21.04	1061.5	26.60		20	0.06143
6	481.15	21.14	1149.2	29.23		10	0.06354
7	441.80	20.80	1020.2	25.32		20	0.06014
8	433.07	20.93	1004.5	25.08	—	15	0.06085
9	441.30	21.00	1017.1	25.21	—	20	0.05998
10	434.25	21.28	1008.9	25.24	—	20	0 06113
11	438.66	21.52	1019.4	25.50	—	19	0.06113
12	437.30	21.20	1013.1	25 26	—	19	0.06070
13	468.20	20.96	1117.2	28.45	—	10	0.06361
14	468.10	21.28	1123.0	28.75	—	10	0.06434
15	467.9	21.20	1112.4	28.24	—	9	0.06323
16	454.90	20.80	1068.9	26.90	—	20	0.06197
17	454.50	21.10	1067.6	26.87	—	19	0.06200
18	405.30	21.00	935.2	23.37	—	20	0.06082
19	367.20	21.20	835.0	20.79	—	17	0.06009
20	520.70	21.10	1273.4	32.88	—	$2^1/_2$	0.06581
21	455.10	21.40	1073.1	27.12	—	$2^1/_2$	0.06252
22	351.40	20.95	798.8	19.95	—	4	0.06037
23	382.90	21.20	884.6	22.26	—	$4^1/_2$	0.06154
24	382.90	20.90	876.0	21.83	—	5	0.06029
25	426.10	21.20	983.2	24.47	—	5	0.06043
26	425.70	20.95	981.9	24.41	—	5	0.06032
27	542.10	21.10	1335.3	34.59	—	1	0.06639
28	491.50	21.40	1193.8	30.78	—	$1^1/_2$	0.06548
29	475.36	21.11	1131 3	28.71	—	$1^1/_2$	0.06319
30	486.8	21.40	1173.2	30.07	—	$1^1/_2$	0.06462
31	488.80	21.10	1174.5	30.00	—	$1^1/_2$	0.06414
32	486.80	20.90	1169.2	29.85	—	1	0.06407
33	492.20	20.80	1188.0	30.43	—	$1^1/_2$	0.06456
34	495.20	20.70	1193.1	30.49	—	1	0.06425
35	500.05	21.21	1207.4	30.92	—	$1^1/_2$	0.06458
36	570.54	21.04	1421.1	37.00	—	$1^1/_2$	0.06733
37	505.10	20.90	1220.6	31.24	—	1	0 06452

TABLE II. (*Continued*).

The mean Specific Heats $\bar{c}_p$ of Didymium between 20° and 600° C.

Sequence-number of the Experiments:	Temperature t in °Cent.:	Final temperature t' of the Calorimeter:	Increase of the temperature $\triangle t$ in μV:	Quantity of Heat Q delivered between $t°$ and t' by 1 Gr. of the substance in Calories:	Quantity of Heat Q_{20} given off between $t°$ and 20° C. by 1 Gr. of the substance in Calories:	Time τ in Minutes, necessary for reaching the maximum Calorimeter temp.:	Mean Specific Heats $\bar{c}_p$ between $t°$ and t' in Calories:
38	591.00	21.30	1496.5	39.42	—	1	0.06919
39	492.5	21.00	1179.7	30.02	—	1	0.06368
40	492.34	20 74	1180.7	30.07	—	1	0.06376
41	585.30	20.95	1477.8	38.84	—	1	0.06883
42	557.07	21.01	1379.2	35.80	—	1	0.06678
43	580.08	21.05	1458.6	38.25	—	1	0.06842
44	575.27	21.05	1441.9	37.73	—	1	0.06808
45	570.25	21.05	1422.5	37.09	—	1	0.06753
46	572.4	21.20	1431.0	37.37	—	1	0.06780
47	567.7	21.10	1412.9	36.78	—	1	0.06729
48	564.93	21.05	1403.2	36.48	—	1	0.06707
49	510.63	20.96	1233.6	31.54	—	1	0.06440
50	515.28	20.94	1245.0	31.81	—	1	0.06434
51	512.61	21.14	1236.5	31.57	—	1	0.06423
52	525.1	21.00	1272.9	32.57	—	1	0.06461
53	540.17	20.99	1315.9	33.75	—	1	0.06500
54	559.95	20.99	1394.2	36.35	—	1 1/2	0.06743
55	582.54	20.96	1457.0	38.01	—	1	0.06769
56	592.3	21.00	1499.5	39.47	—	1	0.06909
57	582.47	21.06	1459 5	38.14	—	1	0.06793
58	351.76	20.79	793.7	19.68	19.72	1 1/2	0.05945
59	408.7	20.7	934.3	23.11	23.16	1 1/2	0.05957
60	433.0	20.80	995.0	24.61	24.66	1 1/2	0.05970
61	457.7	20.80	1063.2	26.46	—	1 1/2	0.06055
62	480.0	20.80	1017.2	28.66	28.71	1	0.06242
63	385.16	20.69	876.8	21.72	21 77	1 1/2	0.05960
64	448.00	20.74	1034.0	25.62	—	1 1/2	0.05995
65	492.5	20.80	1171.9	29.64	29.69	1 1/2	0.06283
66	510.36	21.06	1223.7	31.07	31.14	1 1/2	0.06350
67	540.0	21.00	1310.8	33.51	33.57	1 1/2	0.06457
68	560.0	21.0	1371.8	35.26	35.32	1 1/2	0.06541
69	572.57	20.97	1416.9	36.67	—	1 1/2	0.06649
70	467.75	20.80	1101.5	27.71	—	1 1/2	0.06198
71	452.9	20.80	1049.6	26.08	—	1 1/2	0.06036
72	462.2	20.80	1079.2	26.95	—	2	0.06107
73	321.4	20.60	718.0	17.78	—	2	0.05909

and its subsequent disappearance on further heating, is completely analogous to what was previously observed by us in the case of *zirconium*. As to the separate measurements, attention must be drawn to the following facts. From figure 3 it appears that the points 1—4 initially obtained are situated upon a regular curve PFQ; the time τ in these experiments never

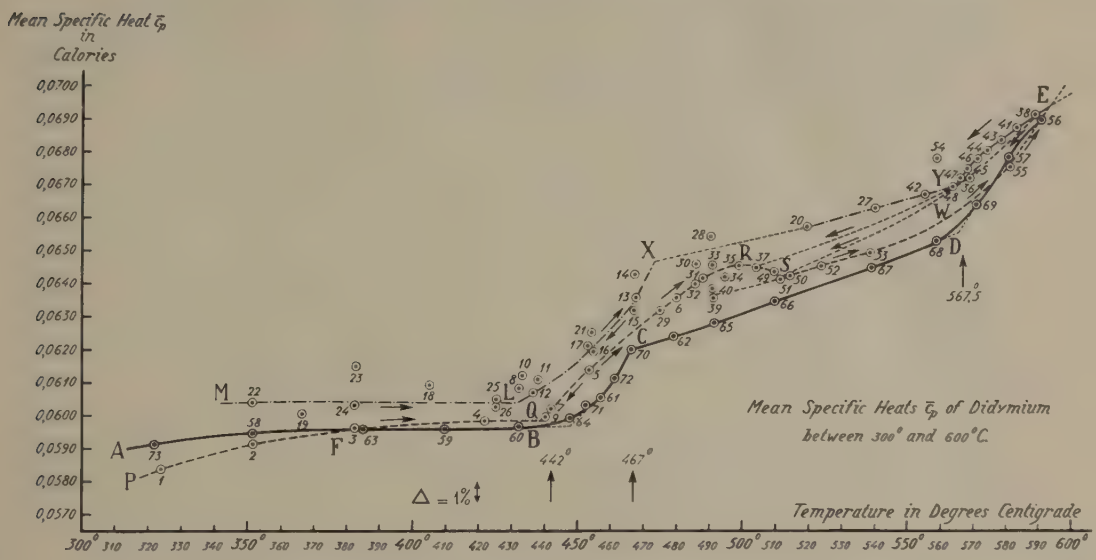

Fig. 3. *The Mean Specific Heats of Didymium between 300° and 600° C.*

exceeded 6 minutes. At about 440° (Q) evidently a thorough change of the inner state of the metal sets in, as is illustrated not only by the sudden change in the inclination of the curve 5—7 with respect to PF, but also by τ now having been changed from 6 to no less than 15—20 minutes. This time τ subsequently shows the trend to augment to 20 minutes maximally. Endeavouring to fix the transition-point Q more accurately, we thus found that point 7 was equally situated on the curve; therefore, now the measurements were continued at temperatures below 440° C. The points 8, 10, 11 and 12, however, all proved to be situated about 2 % higher than was expected, whilst τ still remained 20 minutes, instead of falling back to the initial value of 6 minutes. After these heatings, therefore, neither the points 8—12, nor 5—7 could any longer be reproduced, — as may be seen from the data 13—17: in the measurements 13—15, τ decreased to 10 minutes, but in the experiments 16—19 it again was found to be always 20 minutes. However, as soon as the sample once was heated at 520° C. (N°. 20), τ suddenly proved to drop to 2,5 minutes, and this small value of the time τ remained, — with a tendency slightly to increase, — also in the experiments Nos 21—26, the results of which evidently are scattered in a quite irregular way. We now tried to "stabilize" the inner condition of het metal by heating it at 545° C. (N°. 27). Although, as we shall see, also this time *no* complete stabilization occurred at this

temperature, yet a most curious phenomenon here manifested itself in so far as the time τ suddenly appeared to drop to the *extremely low* value of 1 minute. This value is lower than ever was met with before, even in the case of a lump of *silver*, in which τ never was less than 2 minutes under the same circumstances, although the thermal conductivity of *Ag* is appreciably greater than that of $(Pt + Di)$. This fact once more clearly demonstrates that the speed of heat-delivery to the calorimeter-block depends predominantly upon some still undefined peculiarity of the inner state of the heated metal, much more than upon its thermal conductivity. It corroborates our long-fostered idea that the variations of τ are, indeed, a most trustworthy indication of inner changes occurring in the metals studied, as we have already repeatedly emphasized. Most remarkable is the fact that this very small value of τ now remained preserved in *all* subsequent experiments, — even in those made at the lower temperatures. However, the scattering of the values of c_p still present, proves that *no complete* inner stabilization really yet had taken place: the data subsequently obtained: Nos 28—35 are, indeed, still distributed in a quite irregular way. Therefore, the sample was once more heated at still higher temperatures (Nos 36—38); after the latter heating (N°. 38) the points 38—48 subsequently obtained now proved to be situated on a perfectly smooth curve, but afterwards it was stated that the points 49—54 were not situated on the curve: 20 — 27 — 42 — 48. After heating at 515° C. (N°. 50), the substance was accidentally left at 18° C. during four weeks: now again some inner transformation proved to have occurred in the metal, for, — although point 51 was located quite near to 49 and 50, — the curve *Y E* could *not* be reproduced, the points 52 and 53 now being situated on a curve *W*, which lies appreciably lower. However, after having heated the sample at 590° C. (N°. 56), the metal suddenly proved to have reached a perfectly *stable* condition: now all points subsequently determined were really found to be quite reproducible and to fit in the fully-drawn curve *F B C E* in Fig. 3, with its typical transition-interval between 440° and 467° C. and its rather sharp transition-point at 567,5° C. These values remained always the same, even after heating at a constant temperature for a very long time. The phenomena described are, most probably, connected with the establishment of equilibria between the different kinds of mixed crystals at their transition-temperatures, which, of course, are always accompanied by changes in their stoechiometrical compositions.

§ 5. The parts of the curve between 340° and 440° C., between 467° and 560° and between 575° and 595° C. may be considered as practically linear; within the first interval mentioned c_p almost imperceptibly changes with the temperature. In the said temperature-intervals the *true* specific and "atomic" heats (apparent atomic weight = 141,9) can, therefore, be calculated with a fair degree of accuracy: between 340° and 440° C. c_p and C_p evidently are almost *constant*.

The results obtained are as follows:

1. Between 340° and 440° C. c_p can readily be expressed by the formula:

$c_p = 0{,}05941 + 0{,}16 \,.\, 10^{-5} \,.\, (t - 340)$, and C_p, therefore, by:
$C_p = 8{,}430 + 0{,}227 \,.\, 10^{-3} \,.\, (t - 340)$,
so that in this interval C_p only changes from 8,430 to 8,453 calories.

2. Between 467° and 560° C., c_p may be calculated from:
$c_p = 0{,}06200 + 0{,}366 \,.\, 10^{-4} \,.\, (t - 467)$
and C_p, therefore, from:
$C_p = 8{,}798 + 0{,}5193 \,.\, 10^{-2} \,.\, (t - 467)$, which yields
for C_p the value: 8,798 at 467° C. and 9,281 at 560° C.

3. Between 575° and 600° C., c_p can, with a good approximation, readily be represented by:
$c_p = 0{,}0665 + 0{,}14 \,.\, 10^{-3} \,(t - 575)$, and C_p, therefore, by:
$C_p = 9{,}460 + 0{,}01986 \,.\, (t - 575)$.

Thus for 575° C_p has the value: 9,460 and for 600° C.: 9,956.

It must, however, be emphasized that during our experiments suspicion arose that the $\bar{c}_p$-t-curve above 600° C. probably once more will change its direction, so that the interval of 575°—595° C. here considered perhaps may have the character of a "transition"-interval. In that case the high "apparent" values of C_p could readily be explained and no real physical significance could be attributed to them, because they would relate only to quite *in*determined inner conditions of the metal within this interval.

Evidently *didymium*, — and the same is true for its components: *praseodymium* and *neodymium*, — shows values of its atomic heats which, even at moderate temperatures, appreciably surpass the theoretical limit or $3R$ calories. In this respect they behave just like *cerium* and *lanthanum*.

Groningen, Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — *On Pterotactic Derivatives of Bivalent Platinum with Optically-active, Cyclic trans-1-2-Diamines.* By F. M. JAEGER and J. TER BERG.

(Communicated at the meeting of May 29, 1937.)

§ 1. In this paper a series of complex salts of *bi*valent *platinum* with racemic and optically active *cyclopentane-trans-1-2-diamines* and *cyclohexane-trans-1-2-diamines* are described, which probably present some structural peculiarities hitherto not met with in such compounds.

For the preparation of these salts of bivalent *platinum*, 12 grammes of K_2PtCl_4 are dissolved on the water-bath in as little hot water as possible and then 6 grammes of the base are added to the solution. After some moments the red colour of the latter disappears and a heavy, orange-yellowish precipitate is formed; this is the very sparely soluble compound containing only 1 molecule of the base. When adding to the solution still 3 grammes of the base, the precipitate is, after heating the solution in a closed flask on the water-bath during many hours, finally dissolved to a yellowish coloured liquor. This is filtered and left standing for some time; then the cooled solution is mixed with about 800 cc of alcohol. The salt is slowly precipitated as a white crystalline powder; after 24 hours it is filtered off and recrystallized from as little boiling water as possible. The alcoholic mother-liquor, after being neutralized with *HCl*, is evaporated on the water-bath and, besides *KCl* and the hydrochloride of the base present in excess, still yields a certain quantity of the impure compound, which can be purified by repeated crystallizations from boiling water. In the reactions with the *optically active* bases only *one* salt is generated, with a yield about equal to the calculated quantity. The pure salts thus obtained are perfectly colourless; the derivatives of the optically active bases, in general, prove better to crystallize than those obtained from the racemic bases. The latter *platinum*-compounds originally appear to be deposited as opaque, small spherolithes, which under the microscope appear as aggregates of ten or twelve round-edged individuals without definite forms and only weakly birefracting. Often the rounded lumps have a more flattened, more or less irregularly tabular aspect.

§ 2. On the other hand the salts containing two molecules of the optically-active bases immediately crystallize from their aqueous solutions in the shape of small, lustrous, colourless, apparently quadratic plates. A more detailed study revealed that they are not tetragonal, but truly *rhombic-*

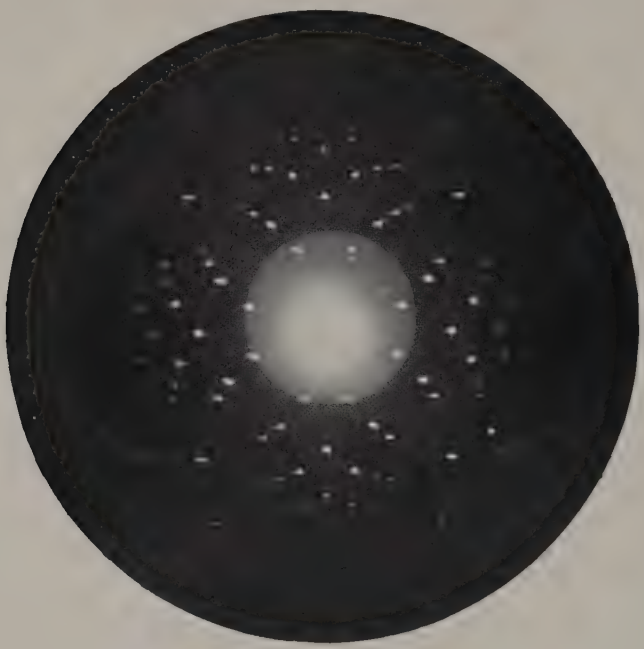

Fig. 1a. *X-ray Pattern of D-{Pt (l-Cptn)$_2$}Cl$_2$ perpendicular to {001}; (tungsten-K-α-radiation) 35 K.V.*

Fig. 1b. *X-ray Pattern of D-{Pt (l-Chxn)$_2$}Cl$_2$ perpendicular to {001}; (tungsten-K-α-radiation) 35 K.V.*

bisphenoidal and *pseudo-tetragonal* to such a degree that their axial ratio: $a : b$ cannot be distinguished from *unity* and that their deviation from true tetragonal symmetry is, in their LAUE-ray patterns perpendicular to {001}, either not at all, or only manifested by the mere presence or absence of a few diffraction-spots in the zones closely situated round the central spot. The two diffraction-patterns of this kind reproduced in Figs. 1*a* and 1*b* of the Plate clearly demonstrate the only small deviations from a perfectly tetragonal symmetry and also the close analogy in the architecture of these crystals, which evidently must be considered as truly *isomorphous*, — as also had already been deduced from the crystallographical measurements. The patterns were obtained with *tungsten*-radiation (35 Kilovolts); they here appear on the same scale (distance of film to crystal = 5 c.M.). Evidently the first pattern does *not* manifest any observable deviation at all from true tetragonal symmetry.

The salts crystallize in the form of Fig. 2.

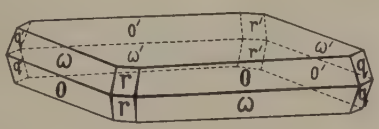

Fig. 2. *Crystalform of D-{Pt(l-Cptn)$_2$}Cl$_2$ and of D-{Pt(l-Chxn)$_2$}Cl$_2$.*

D-{$Pt(l\text{-}Cptn)_2$}Cl_2 has the axial ratio : $a : b : c = 1 : 1 : 2{,}937$.

The forms observed are: $c = \{001\}$, large and lustrous;

$o = \{111\}$ and $\omega = \{1\bar{1}1\}$, narrow, about equally developed;

$r = \{101\}$ and $q = \{011\}$, both small, equally developed an well measurable.

Angular Values:

$$c : r = (001) : (101) = 71° 12'.$$
$$c : r = (001) : (111) = 76° 28'.$$

The crystals are optically biaxial, but D-{$Pt(l\text{-}Cptn)_2$}Cl_2 is almost uniaxial : the plane of the optical axes is {100}, with the *c*-axis as the first bisectrix of positive character. The apparent angle of the axes is very small.

A perfect cleavability occurs parallel to {001}. By means of oscillation-spectrograms, the parameters of the elementary cell were determined to be : $a_0 = b_0 = 8{,}10$ Å.U.; $c_0 = 23{,}5$ Å.U. The cell contains 4 times the molecular mass; the specific gravity of the crystals is: 2,061.

D-{$Pt(l\text{-}Chxn)_2$}Cl_2 has the axial ratio: $a : b : c = 1 : 1 : 3{,}163$, with the same limiting faces as the former salt. The angular values are : $(001) : (111) = 77° 24'$ and $(111) : (1\bar{1}1) = 87° 16\frac{1}{2}'$. The plane of the optical axes is {100}; the angle of the axes is small, but greater than in the first case. The *c*-axis is the first bisectrix; the double-refraction is positive, the

dispersion of rhombic character: $\varrho < \nu$. The crystals are perfectly cleavable parallel to {001}.

From X-ray spectrograms round the principal axes, the parameters of the elementary cell, which contains 4 molecules of the salt, were calculated to be: $a_0 = b_0 = 8{,}10$ Å.U.; $c_0 = 25{,}2$ Å.U. The density is: 1,952.

§ 3. In solution the two salts are strongly *dextro*gyratory for all wavelengths between 4200 and 7000 Å.U.; i.e. their rotation is *opposite* to that of the bases present in their complex ions.

The molecular rotations $[M] \cdot 10^{-2}$ of these salts, together with those of the free bases of *opposite* rotation [1]), are graphically represented in Fig. 3.

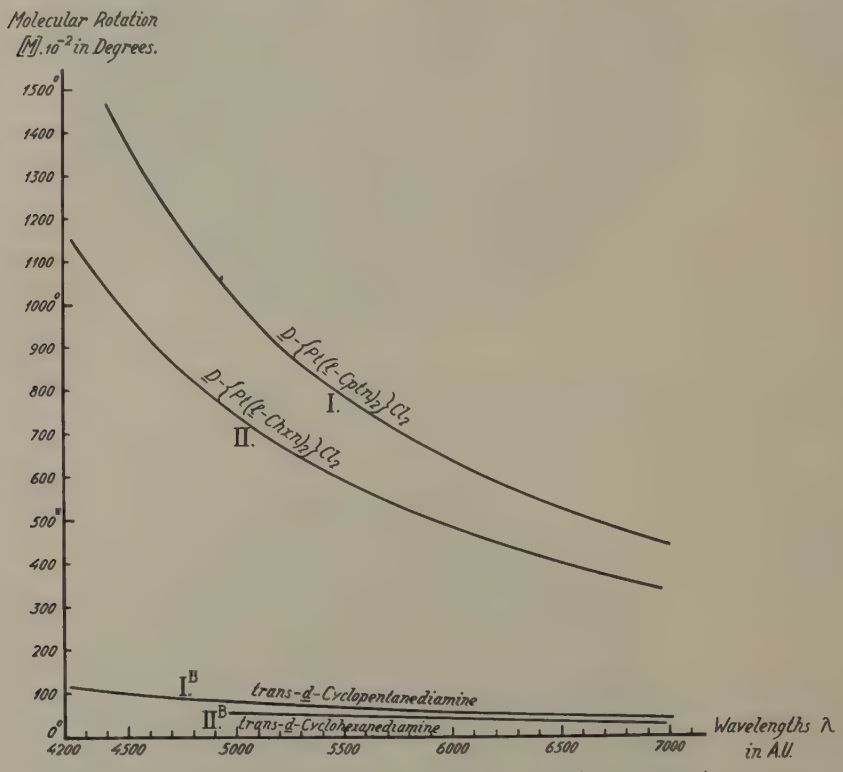

Fig. 3. *The Molecular Rotations* $[M] \cdot 10^{-2}$ *of D-*$\{Pt\ (l\text{-}Cptn)_2\}\ Cl_2$ *and D-*$\{Pt\ (l\text{-}Chxn)_2\}\ Cl_2$ *a d of d-Cyclopentane- and d-Cyclohexane-diamines.*

§ 4. From these data it at once becomes clear that the rotation of these salts is not only opposite to that of the bases contained in them, but that this opposite rotation is also *appreciably* greater than that of the free diamines themselves; their rotatory influence in the complex ion appears at different wavelengths to be enlarged in a ratio of at least about 13 to 15

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[1]) F. M. JAEGER and L. BIJKERK, these Proceed., **40**, 12, 22, (1937); F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chemie, **175**, 168, 169, (1928).

Rotatory Dispersion of Di-*l*-Cyclopentanediamine- and of Di-*l*-Cyclohexanediamine-Plato-Chlorides in Aqueous Solution.

Wavelength λ in A.U.:	Specific Rotation $[\alpha]$ of $D\text{-}\{Pt(l\text{-}Cptn)_2\}Cl_2$:	Molecular Rotation $[M] \cdot 10^{-2}$ of $D\text{-}\{Pt(l\text{-}Cptn)_2\}Cl_2$:	Specific Rotation $[\alpha]$ of $D\text{-}\{Pt\ (l\ Chxn)_2\}Cl_2$:	Molecular Rotation $[M] \cdot 10^{-2}$ of $D\text{-}\{Pt\ (l\text{-}Chxn)_2\}Cl_2$:
6980	+88.3°	+443°	+68.3°	+337°
6730	97.7	490	75.3	372
6480	107.0	532	82.4	407
6262	115.0	577	89.3	441
6074	124.0	622	95.8	473
5893	133.6	667	102.1	504
5735	142.1	712	109.1	539
5592	150.3	757	115.9	573
5463	159.8	802	122.8	607
5340	169.4	850	129.2	638
5224	179.6	899	135.9	671
5126	189.0	948	142.6	705
5036	199.2	996	149.2	737
4950	208.7	1045	155.7	769
4862	218.3	1094	161.6	798
4793	227.8	1142	167.7	828
4724	236.4	1188	173.7	858
4658	245.9	1232	181.3	896
4596	254.9	1280	186.9	923
4537	264.4	1328	193.3	955
4483	276.1	1377	200.1	988
4430	283 4	1426	205.9	1017
4380	—	—	212.3	1048
4335	—	—	216.7	1070
4290	—	—	223.3	1103
4248	—	—	232.4	1148

The salts: $L\text{-}\{Pt\ d\text{-}Cptn)_2\}Cl_2$ and $L\text{-}\{Pt\ (d\text{-}Chxn)_2\}Cl_2$ show the same rotations, but with opposite algebraic signs.

times by the linkage of these bases into the atomic cycles including the central *platinum* atom.

Now the two bases are *trans*-substitution-products, as is proved by their resolvability into optical antipodes: this means that the two NH_2-groups are situated at *opposite* sides of the mean plane of the carbon-rings. In the case of the *cyclohexanediamine* with its *puckered* carbon-cycle, there are at least two ways in which the molecule can be attached to the central atom; but *cyclopentanediamine*, having a *flat* carbon-cycle, can only be linked to it in a single way. Even if the four valencies of the bivalent *platinum*-atom, according to WERNER's original hypothesis, are supposed to be situated *in the same plane*, — the two molecules of the *cyclopentanediamine* must be inserted into the complex ion in an *oblique* position, twisted with respect to each other like the wings of a stirrer or propeller; and the ion as such will thus have a single binary axis of symmetry perpendicular to the plane of the four valencies of the *platinum*-atom and two binary axes in that plane, bisecting the right angles between those four *Pt*-valencies. This is exactly the symmetry of the rhombic-bisphenoidal class.

The special way of linkage here described of the two cyclic systems to the central metallic atom, may be indicated as a *pterotactic* [1]) one and has to be distinguished from the "spirane" like structures, as observed in carbon-compounds. Such a pterotactic arrangement lowers the degree of symmetry of the complex ion in such a way that all planes of symmetry necessarily must disappear and the whole architecture only can preserve an *axial* symmetry. This axial symmetry is in full agreement with the strong optical activity exhibited by the ion and with the *exclusive* generation of only a single, optically active compound in the evidently "dissymetrical" reaction between K_2PtCl_4 and the dextro- or levogyratory bases used. Taking into account the fact of the complete analogy, of the crystal forms of the *dicyclopentanediamine-* and *dicyclohexanediamine-plato*-derivatives as well as of their *X*-ray patterns, — it is evident that the two kinds of complex salts also possess *the same* structural character of their cations; i.e. it can be considered as certain that the way of insertion of the two cyclic bases into each of those complex ions has occurred in exactly the same way. Thus the *dicyclohexanediamine-plato-chloride* also must be considered to be a typical "pterotactic" compound and its rotatory properties are, therefore, quite analogous to those of the *dicyclopentanediamine* salt previously dealt with.

§ 5. The salts of this pterotactic type: $D\text{-}\{Pt(l\text{-}Base)_2\}Cl_2$ and $L\text{-}\{Pt(d\text{-}Base)_2\}Cl_2$, if combined in equimolar quantities, will yield a *racemic* compound of the constitution:
$[D\text{-}\{Pt(l\text{-}Base)_2\}Cl_2 + L\text{-}\{Pt(d\text{-}Base)_2\}Cl_2]$; this true racemate will, of course, by appropriate means, be resolvable into its optical antipodes.

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[1]) From: *pteron* = wing and *tattein* = arrange.

By means of X-ray experiments it could, moreover, be proved beyond any doubt that this "racemate" and the optically *in*active product, which was obtained by the direct interaction between K_2PtCl_4 and the *racemic* base, are indeed rigorously *identical*. These racemates obtained from the *in*active *cyclohexane-* and the *cyclopentanediamines*, — juist like the optically active salts of the two bases with respect to each other, — also proved to be quite isomorphous.

Their *d-tartrates* could be obtained as crystalline products which, however, hitherto could not be separated into fractions of different solubility and specific rotation, so as to lead to a direct fission into their antipodes.

The *d-tartrate* obtained is very soluble; but on slow evaporation of the solution it readily crystallizes. Small, opaque crystals, which soon loose their water of crystallization.

Monoclinic-sphenoïdal.

$a : b : c = 0{,}688 : 1 : 1{,}528$;

$\beta = 46° 12'$.

Forms observed: $m = \{110\}$ and $\{p = \{1\bar{1}0\}$, also $c = \{001\}$, about equally large; $q = \{011\}$ and $r' = \{\bar{1}01\}$ well developed; $\omega' = \{\bar{1}11\}$, smaller than q; $t = \{0\bar{1}1\}$, often absent or small; $s' = \{\bar{1}03\}$, small; $x' = \{\bar{1}\bar{1}3\}$, somewhat larger than s'; $o = \{\bar{1}\bar{1}1\}$, mostly absent, small. (Fig. 4).

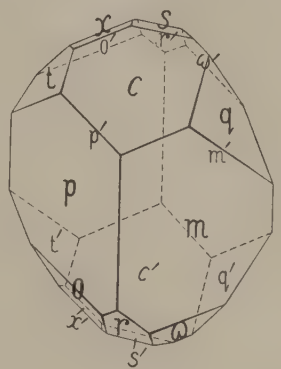

Fig. 4. *Crystalform of* $\{Pt(r.Chxn)_2\}d\text{-}C_4H_4O_6 + \frac{1}{2}H_2O$

Angular Values:	*Observed*:	*Calculated*:
$c : s' = (001) : (\bar{1}03) =$	*47° 38′	—
$s' : r' = (\bar{1}03) : (\bar{1}01) =$	*60 54	—
$m : p = (110) : (1\bar{1}0) =$	*52 50	—
$m : c = (110) : (001) =$	51 32	51° 18′
$m : s' = (110) : (\bar{1}03) =$	93 50	93 26
$s' : x' = (\bar{1}03) : (\bar{1}\bar{1}3) =$	26 55	26 57
$c : q = (001) : (011) =$	47 24	47 48
$c : \omega' = (001) : (\bar{1}11) =$	105 22	105 26
$r' : o' = (\bar{1}01) : (\bar{1}\bar{1}1) =$	33 0	33 7

The angular values oscillate considerably, often about 0°,5.
No distinct cleavability was observed.

§ 6. However, still another optically *in*active compound has, — from the theoretical point of view, — to be expected, in which one molecule of the *dextro-* and one molecule of the *levo*gyratory base simultaneously may be

present: then the planes of the two pterotactically linked molecules necessarily would be *equally* inclined and directed with respect to the plane of the four *Pt*-valencies and, therefore, this time within the complex ions will be inclined in *the same* sense. This ion thus should possess a plane of symmetry Σ perpendicular to the plane of the four *Pt*-valencies and, therefore, it could by no means ever be resolved into optically active components. The new inactive salt in this respect thus would completely behave like *meso-* (or *anti-*)*-tartaric acid* in comparison to the resolvable *racemic acid*. One could expect that perhaps it might be generated, if the *racemic* bases were made to react with K_2PtCl_4, — at least when it is supposed that there is no particular reason of stability, which presumably would exclude the possibility of simultaneous introduction of a dextro- and a levogyratory molecule into one and the same complex ion, — as such a hindrance certainly was stated by us [1]) to exist in the case of the *tridiamino-cobaltic* salts of the optically active diamines under consideration. In the latter case such kind of "mixed" ions, — if generated at all, — proved in solution always to be decomposed into a mixture of the corresponding salts containing three molecules of only the bases with *the same* direction of rotation. In this case the resolvable *in*active compounds could be demonstrated also to be built up from the *D*- and *L*-antipodes when combined in equal number of molecules. As, however, at least in principle, there is *no* such opposite tendency to a simultaneous introduction of two molecules of oppositely rotating bases into the same complex ion present, — we must conclude that, in the case of the pterotactical linkage of such diamines, the possible existence of *four* isomerides must be taken into account: namely the *D*- and *L*-salts already described, the resolvable *racemate* of the latter und the *un*resolvable *meso*-form just mentioned.

Because the inactive reaction-product of the racemic base with K_2PtCl_4 proved to be identical with the true racemate generated by mixing equimolar quantities of the *D*- and *L*-compounds, evidently there was no chance of catching this expected *meso*-form in the two ways described.

§ 7. The only way still possible for trying the preparation of $\left\{Pt\begin{pmatrix} d\text{-}Chxn \\ l\text{-}Chxn \end{pmatrix}\right\}Cl_2$ was heating K_2PtCl_4 with half the calculated quantity of *d-cyclohexanediamine* and separating this product from the reaction-mixture, then subsequently heating this purified product with exactly the calculated quantity of *l-cyclohexanediamine* in aqueous solution and precipitating the product now generated by means of an excess of absolute alcohol. Thus a wite, crystalline salt was obtained, which was recrystallized from as little water of 80 C. as possible, by slow evaporation of the saturated solution at room-temperature. First crystallized the typical

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[1]) F. M. JAEGER and L. BIJKERK, these Proceed., **40**, 256, 325, (1937).

spherolithes and flat, rounded aggregations already described, which evidently represented the anhydrous racemic salt previously mentioned: its identity with the racemate, as well as with the $\{Pt(rac.Chxn)_2\}Cl_2$ obtained from the racemic base, was, moreover, demonstrated by means of its *X*-ray spectrogram. After some days *another* colourless salt started to crystallize from the mother-liquor in small, parallelogram-shaped tables and in well-developed thicker crystals. They were separated from the solution and found to be optically *in*active in solution. On analysis they proved to yield:

Pt: 32,76—32,80 %; *N*: 9,52—9,62 %; H_2O: 17,82 %; *Cl*: 11,73 %.

Evidently, the composition of this salt is: $\{Pt(rac.Chxn_2\}Cl_2 + 6H_2O$; calculated: 32,42 % *Pt*; 9,30 % *N*; 17.94 % H_2O and 11,79 %. In solution it does not manifest any optical rotation.

The compound, on measurement with the theodolite-goniometer, proved to be *triclinic-pinacoidal.*

The compound crystallizes in small colourless and lustrous crystals which usually are tabular parallel to {001}.

Triclinic-pinacoidal.

$a : b : c = 0{,}891 : 1 : 0{,}987.$

$A = 84°48'$; $\alpha = 98°26'$
$B = 77\ 15$; $\beta = 104\ 21$
$C = 102\ 42$; $\gamma = 75\ 41$

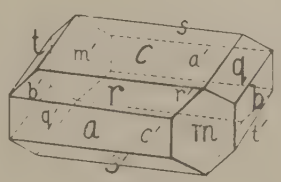

Fig. 5.
Rac. $\{Pt(Chxn)_2\}Cl_2 + 6\,H_2O$.

Forms observed:

$a = \{100\}$; $b = \{010\}$; $c = \{001\}$, the latter form often predominant, so that the crystals are parallelogram-shaped; $r = \{101\}$; $s = \{\bar{1}01\}$; $q = \{011\}$; $t = \{0\bar{1}1\}$; $m = \{110\}$; $M = \{1\bar{1}0\}$; all about equally broad.

Angular Values:	*Observed*:	*Calculated*:
$b : m = (010) : (110) =$	*56° 10′	—
$m : a = (110) : (100) =$	*46 32	—
$a : c = (100) : (001) =$	*77 15	—
$c : b = (001) : (010) =$	*84 48	—
$b' : t = (0\bar{1}0) : (0\bar{1}1) =$	*47 59	—
$a : M = (100) : (1\bar{1}0) =$	35 34	35° 34′
$a : r = (100) : (101) =$	35 43	35 50
$c : m = (001) : (110) =$	75 18	75 12
$c : M = (001) : (1\bar{1}0) =$	84 31	84 26
$c : s = (001) : (\bar{1}01) =$	55 52	55 47
$b' : q = (010) : (011) =$	42 40	42 43
$b : s = (010) : (\bar{1}01) =$	75 24	75 15

No distinct cleavability was observed.

On {001} the extinction is oblique: about 40°—42° with respect to the direction of the *b*-axis; one dark hyperbola is eccentrically visible.

After carefully dehydrating the salt, an *X*-ray spectrogram was made of the remaining white anhydrous powder: this proved to be *completely identical* with the spectrograms obtained with the two optically inactive salts previously prepared. From this the conclusion must be drawn that, beyond any doubt, the triclinic salt described solely represents an *hexahydrate of the racemic compound* and consequently *is not* the *meso*-salt here looked for.

Evidently, therefore, also in this case the simultaneous introduction of two molecules of the oppositely rotating bases into the complex ion seems to be impossible under the circumstances mentioned: in solution two molecules of the salt obtained immediately prove to be changed into an equimolecular mixture of the corresponding salts with two dextro- and two levogyratory molecules of the base respectively.

Physical Chemistry of the University.
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Chemistry. — *The constitution of toxoflavin.* (Provisional communication.) By A. G. VAN VEEN and J. K. BAARS.

(Communicated at the meeting of May 29, 1937.)

Some years ago we described the isolation and properties of toxoflavin [1], one of the two very violent poisons that can be formed by the action of Bacterium cocovenenans. This bacterium, which was discovered by MERTENS and VAN VEEN, is the cause of the well-known bongkrek- and semaji-poisonings met with in Java.

Toxoflavin crystallises in yellow needles, melts at 171° and gives an intensely yellow-coloured solution in water. The aqueous solution has a neutral reaction and is stable only between pH_3 and pH_8. By the action of sulphite and other reducing agents, toxoflavin is reduced to a colourless compound; after shaking with air the yellow colour returns. The substance is very stable to bromine, nitric acid, nitrous acid, and other oxidants and possesses no NH_2- or other reactive groups.

The pharmacological investigation on rabbits was made by DARWIS AMAR and A. GREVENSTUK [2] who showed that toxoflavin is a violent

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[1] A. G. VAN VEEN and W. K. MERTENS. Proceedings Royal Acad. Amsterdam **36**. 666, (1933); Rec. Trav. Chim. **53**, 257, 398 (1934).

[2] Geneesk. Tijdschr. v. N. I. **75**, 104 (1935).

heart poison, 0.4 to 0,5 mg. of the substance injected subcutaneously being a fatal dose for a rabbit of 1.5 to 2.0 K^0. The heart becomes strongly congested with blood and very much resembles the beri-beri heart described by WENCKEBACH.

Struck by its intensive yellow colour, green fluorescence, (which actually in the purest preparations is extremely weak), reversible reducibility, absorption spectrum and stability to various oxidising reagents, we considered at the time that toxoflavin, $C_6H_6N_4O_2$, belonged to the lyochromes, a class of substances discovered at about the same time and to which belongs lactoflavin, a component of vitamine-B_2.

Toxoflavin shows great similarity in properties with lumi-lacto-flavin, the irradiation-product of lactoflavin, and like this substance possesses a substituted alloxan nucleus and a methylimid group, but when treated with baryta does not split off urea.

When it was subsequently shown that lumi-lactoflavin was actually an iso-alloxazine derivative, it was at once clear that toxoflavin, which does not possess a benzene nucleus, could not be regarded as a lower homologue of lumi-lactoflavin.

As the result of a series of experiments, we concluded that toxoflavin (in connection with its property of great reversible reducibility) fulfilled the function of oxygen-conveyor for the bacteria. At the same time we communicated some details on the original toxoflavin-albumen complex. We shall return later to the results obtained by the catalytic reduction of toxoflavin and to the product formed by its reaction with hydrochloric acid.

A welcome contribution to our knowledge of the subject was made as a result of the investigations of K. G. STERN [1]) to whom we had forwarded some material. He investigated the oxidation-reduction potentials of toxoflavin, and found that the normal potential (compared with a normal hydrogen-electrode) at pH_7 amounted to —0.49 volt; toxoflavin forms with its reduction-product between pH_4 and pH_8 a completely reversible system. STERN is also of the opinion that after the complete elucidation of the structure of lumi-lactoflavin, the similarity of this substance with toxoflavin is not so great as appeared to be the case three years ago.

Owing to the small amount of toxoflavin available and to the difficulties of obtaining larger quantities, we have been able to make only slow progress with the investigation of the constitution of this interesting substance.

In our attempts at a systematic degradation of the molecule we were always met by the difficulty, which is not encountered in the case of lactoflavin, that no definite stable grouping, such as a benzene nucleus, is met with in the products. The chief degradation products were always oxalic acid, ammonia, methylamine and mixtures of substances which, owing to the small amounts available and to their tendency to oxidation

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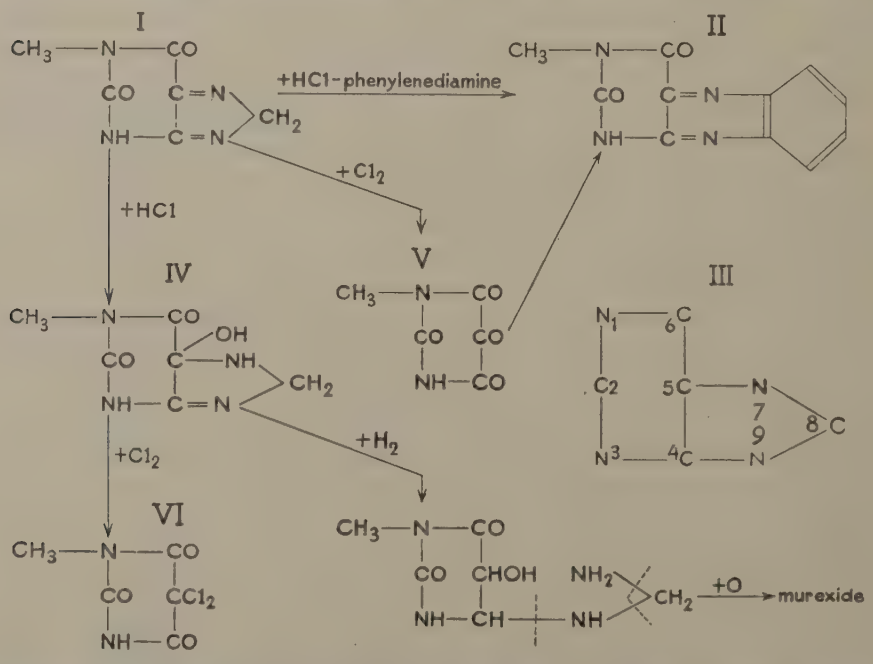
[1]) Bioch. J. **21**, 500 (1935).

in the air, could not be purified. We were thus forced to limit ourselves to a relatively small number of reactions for the purpose of clearing up the constitution. We found that toxoflavin in many cases reacted quite remarkably. In our previous work (l.c.) we gave the analysis for toxoflavin and also for a substance $C_6H_8N_4O_3$ obtained from it by the action of hydrochloric acid and to which we gave the name toxoflavin hydrate. This substance is colourless, crystalline and can be sublimed. It is sparingly soluble in almost all solvents and melts at 250°. In our previous publication we also stated that toxoflavin gave the murexide reaction when treated with potassium chlorate and hydrochloric acid (contrary to our previous statement, toxoflavin hydrate also gives this reaction), which led us to the supposition that a close relationship existed to the purines. The small molecular weight of toxoflavin excluded any relationship to the pterins.

In the following we shall briefly summarise the reactions that led us to the structural formula (I) for toxoflavin. When toxoflavin is slowly oxidised at 50° with potassium chlorate and hydrochloric acid, methyl-alloxan is formed. Analyses were made of the N-methyl-alloxazine, obtained by the condensation of this methylalloxan with ortho-phenylenediamine hydrochloride. Toxoflavin hydrate, in spite of its poor solubility, may also be oxided in this way but yields (N)-methyl-5,5'-dichloro-barbituric acid which was identified as such and also by its reduction to (N)-methyl-



barbituric acid. Both these reactions show that 5 of the 6 carbon atoms are in the pyrimidine nucleus in which are also the two oxygen atoms of the toxoflavin molecule. For, according to E. FISCHER [1]), purine derivatives

[1]) Untersuchungen in der Puringruppe (1882—1906), Berlin, 1907.

with a methine group in the pyrimidine ring, such as hypoxanthine, when oxidised do not give a murexide reaction, or if at all, only with difficulty.

This conclusion was further established by a very remarkable reaction. When concentrated aqueous solutions of toxoflavin and o-phenylenediamine hydrochloride are mixed and warmed gently for a short time, a precipitate of N-methyl-alloxazine is formed in good yield (II). This alloxazine is identical with the analogous condensation product, obtained by the oxidation of theobromine, and also with the above-mentioned methylalloxazine. From this smooth condensation, it appears that the oxygen atoms in the alloxan ring were originally present as such, and it is clear that the methylimid group found in toxoflavin and toxoflavin hydrate has not been formed by a re-arrangement from a methoxyl group but is actually present as such in the molecule. Toxoflavin does not indeed possess a methoxyl, as is also shown when reacted on with ZEISEL's reagent. There are still to be accounted for 2 N-atoms, 1 C-atom and 2 H-atoms. As appears from the above-mentioned reactions, these must be connected with the carbon chain of the pyrimidine ring. As we have seen, these residual N-atoms are very easily split off. This would suggest that both N-atoms are attached to the C-atoms of the alloxan ring. A carbon atom on C_4 or C_5 (see purine-skeleton III) would not be so easily split off, even though under certain circumstances a carbinol- or aminomethyl-group on C_5 can be split off [1]). Actually we were able by degradation to obtain uramil derivatives from toxoflavin-hydrogenation products, which indicates that a nitrogen atom must be attached to C_5. Taking the available valencies into account, there is no other possibility than to assume that these two N-atoms have united to form a ring with the remaining C-atom. In other words, toxoflavin has a purine-skeleton (III)and is an isomer of methylxanthine. If it is assumed to be isomeric with methylxanthine, then the positions of the two double bonds are also established. Purine derivatives usually have one double bond between C_4 and C_5 and a second on C_8 (see III). In the iso-xanthines and iso-uric acids described by BILTZ [2]), one double bond is between atoms 3 and 4 or 4 and 9 or 5 and 7, the second double bond is always attached to atom 8. All these compounds, however, are colourless and do not react (so far as we have been able to determine) with o-phenylenediamine with the formation of alloxazine.

In our opinion the only plausible possibility is the structure represented by formula I. From this we see that toxoflavin is a di-imine in which the two imino-groups are connected to a CH_2 group. In this way toxoflavin exhibits properties reminiscent of alloxan. On the other hand the 5-membered ring has an aromatic character, which explains the great stability towards oxidation. The splitting off of the $=N-CH_2-N=$

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[1]) Treat. B. JOHNSON and A. LITZINGER. Am. Soc. **58**, 1940 (1936).

[2]) H. BILTZ. Die neuere Harnsäurechemie, Leipzig, 1936.

ring by phenylenediamine, with the formation of the much more stable pyrazine system, is easily understandable but is none the less remarkable. Methylenediamine is evidently split off during this reaction and this being a very labile substance decomposes easily into ammonia, formaldehyde (which reacts with more phenylenediamine) and other products. It is thus not surprising that we were unable to identify methylenediamine as being present itself.

The other reactions of toxoflavin are also in agreement with what one would expect from a substance possessing formula I. When an aqueous solution of toxoflavin is treated at 30° with an aqueous SO_2 solution, it becomes almost colourless. If this solution is warmed to 100° with exclusion of air, the original yellow colour of toxoflavin is almost completely restored, but again disappears if the solution is cooled to 0°. This phenomenon is entirely reversible and analogous to the reaction of H_2SO_3 on alloxan, in which addition (at C_5) occurs, the resulting alloxan sulphite decomposing when warmed with the liberation of H_2SO_3. If the substance is treated with a weak alkaline solution of sodium sulphite, at first addition takes place, followed by reduction (the solution remains colourless when warm). Addition of H_2O_2 causes the yellow colour to return. When toxoflavin is treated in aqueous or alcoholic solution with o-phenylenediamine, instead of its hydrochloride, a black-coloured, poorly soluble complex compound is obtained, as is also the case with alloxan.

Under the influence of hydrochloric acid, toxoflavin adds on water easily, forming toxoflavin hydrate (IV); this is analogous to the formation of alloxan hydrate. The ring system remains intact; the murexide reaction remains positive, and there are no amino-groups present, capable of being benzoylated or of reacting with HNO_2, which might have been formed as the result of a possible splitting open of the five-membered ring. Furthermore, any derivatives that could have been formed would have a formamino-side chain which would readily split off formaldehyde; actually however, toxoflavin hydrate is stable to boiling hydrochloric acid. We assume, therefore, that this substance is represented by the configuration IV which agrees with what might be expected to take place during water addition on an alloxan derivative of this type. This also explains the formation of the final product of oxidation obtained by the action of potassium chlorate, namely N-methyl-5,5'-dichlorbarbituric acid (VI), while toxoflavin, when oxidised by this method, yields methylalloxan. All efforts to obtain N-methylxanthine from toxoflavin by isomerising agents, as heat, irradiation, acids, etc., or by dehydration of the hydrate (with shifting of the double bond to C_8) were unsuccessful. This is indeed not surprising, when one realises that in toxoflavin two double bonds instead of one must alter their positions. Moreover, BILTZ (l.c.) has found that, in the case of 4-hydroxy-4-5-dihydro-uric acid (probably due to the transposition of H and OH) and other hydroxy-compounds, it was not possible to split off water, and in these compounds it was not even necessary to effect a

primary migration of the double bond to C_8, as would be necessary in our case with toxoflavin hydrate. There is another great difference between toxoflavin and purine- and iso-purine derivatives so far as they are known.

When toxoflavin is hydrogenated catalytically (in water or acetic acid) in the presence of platinum oxide, two molecules of hydrogen are quickly absorbed. Besides the addition of hydrogen, secondary reactions take place, the five-membered ring also being split open. The opening of this ring is indeed not surprising, as a fully hydrogenated glyoxaline ring is first formed which readily splits off formaldehyde under the influence of acids.

Judging from the course of the slow decoloration of the solution during the addition of hydrogen, one double bond is not reduced before the other (as is the case in sulphite reduction) but the whole molecule is directly and completely hydrogenated. Amongst other products we obtained a substance that could be well sublimed and which gave an analysis agreeing with that required for tetrahydro-toxoflavin. If this is warmed with aqueous hydrochloric acid and evaporated to dryness, a murexide derivative is formed. This is what one would expect after the destruction of a five-membered ring and the subsequent oxidation by air of the resultant uramil derivatives in the presence of ammonia. The same phenomenon is obtained when the hydrogenation product of toxoflavin in water is shaken with air in the presence of the used catalyst.

When toxoflavin hydrate is catalytically hydrogenated in acetic acid, only substances are obtained which in air spontaneously give murexide derivatives. The complex reactions that take place during these hydrogenations may possibly be partly due to the condensation of toxoflavin with its decomposed products of hydrogenation. These hardly soluble condensation products, that are formed during the actual hydrogenation, we hope to discuss fully in a subsequent publication. Their formation also indicates the labile nature of the fully hydrogenated five-ring (especially in the hydrogenated toxoflavin hydrate, which in this respect may be compared with the very labile 5-hydroxy-pseudo-uric acid) and that the substituted alloxan ring has remained intact.

If toxoflavin is treated with concentrated hydro-iodic acid, reduction occurs with separation of iodine. If the resultant solution is evaporated to dryness in a vacuum desiccator, a mixture of substances is obtained which, when exposed to the air in neutral aqueous solution, assumes an intensive purple colour. The partially reduced five-ring is thus destroyed by the action of the strong acid. The five-ring is also easily destroyed when toxoflavin is reduced by sulphite or some other reducing agent, quickly oxidisable uramil derivatives resulting from these reductions.

The alkaline degradation of toxoflavin did not yield useful results, nor did the alkaline oxidation with permanganate. The latter operation, however, yielded a product in good quantity, crystallising in small white needles, which begin to sublime at 120° and melt at 220°. The substance

has the formula $C_6N_5H_7O$, possesses no methylimid and does not give a murexide reaction. Taking into account the high nitrogen content, it must have been formed as a result of the condensation of degradation products from two molecules of toxoflavin, accompanied by the opening of the alloxan ring and the splitting off of the methylimid or methylurea group, etc. In any case this remarkable substance, which is stable to concentrated hydrochloric acid, nitric acid and $KMnO_4$, represents only a secondary reaction product, and is of no direct use as a means to elucidating the constitution of toxoflavin.

The attachment of the methyl group on N-atom I is arbitrary; we hope to decide this point by subsequent work. Finally the question: does the configuration represented by I serve to explain satisfactorily the intensive yellow colour? We believe that it does. Anhydrous alloxan itself has also an intensive yellow colour. In this respect BILTZ refers to the fact that aliphatic α, β, γ-triketones have intensive yellow colours, which disappear during easy hydrate formation. It must also be borne in mind that 1,2-diketones and ortho-quinones frequently have intensive colours [1]). Our opinion is that the colour of toxoflavin may be explained by the fact that this substance is to be regarded as the cyclic di-imine of a triketo-compound. One can, of course, endeavour to explain the colour by assuming that the double bonds in the alloxan ring, caused for example by the enolisation of one of the carbonyls, are in conjugation with the keto-imino groups, or by a 5-valent nitrogen atom, or finally by assuming that the methylimid group was originally present as 2- or 6-methoxyl, in which case one could give the alloxan ring a quinonoid structure. We have already referred to the fact that no OCH_3 group can be detected in toxoflavin, while the final product, resulting from the smooth condensation between toxoflavin and o-phenylenediamine, possesses a methylimid group; consequently methoxyl is quite certainly absent. Of the other possibilities there remains little to be said. The same questions, when applied to uric acid, also open up many possibilities [2]). A 5-valent nitrogen atom is not present in the molecule because toxoflavin shows a neutral reaction and does not form a pseudo-base [3]). These considerations of colour call to mind the blue-red murexide, which is also an alloxan derivative, its colour very often being explained by assuming a quinonoid structure. In the case of murexoin (a murexide in which all 4 nitrogen atoms in the ring have been methylated) such a quinonoid structure is not possible. It occurs to us that one could here usefully apply the betaine-structures proposed by KUHN [4]) which explain better the coloration of various substances, such as quinoline yellow and indigo; the other

[1]) H. BILTZ. B. **45**, 3659 (1913).

[2]) Compare for example H. FROMHERZ and A. HARTMANN B. **69**, 2440 (1936) and H. BILTZ, ibidem 2750.

[3]) J. TAFEL, B **32**, 3194 (1899).

[4]) R. KUHN, Naturwiss. **20**, 618 (1932).

explanation, of the colour only being due to the polyketonic character of the murexide, appears to us to be doubtful. In the case of toxoflavin, however, the polyketonic nature is in our view a sufficient explanation of the yellow colour.

Finally we wish to take this opportunity of expressing our thanks to the Kon. Wilhelmina Jub. Stichting and the Instituut voor Volksvoeding for the financial assistance given for this investigation.

Central Medical Laboratory, Batavia-C., April 1937.

Botany. — *Some remarks on the vegetation on the sandy soil of the Padang Loewai (E. Koetai, E. Borneo).* By O. POSTHUMUS.

(Communicated at the meeting of May 29, 1937.)

The vegetation of the Padang Loewai resembles very much the flora of other regions with a soil, consisting of white, loose sand, as have been described already for the Dutch East Indies by TEYSMANN, POLAK, VAN STEENIS [1]) and others.

Nevertheless the following short notes on the vegetation of the Padang Loewai may be of some interest, because the soil of this „Padang" [2]) was studied in details by HARDON [3]) after some samples, taken by the author on his trip, together with Mr. H. WITKAMP, in October 1930.

The Padang Loewai is situated south of Melak, at the Mahakam river, on a terrace of this river, about 80—90 M above sea-level. Behind Melak the road to the Padang rises rather abruptly to the terrace; along the road the original vegetation has been destroyed by the shifting cultivation (ladangs) of the Dayaks. The vegetation shows here all transitions from that of a newly burned field to a secundary forest. At first Pteridium aquilinum KUHN (2079) [4]) is abundant; afterwards the land is covered by Imperata cylindrica BEAUV., in which Nephrolepis exaltata SCHOTT (2071), Gleichenia linearis CLARKE (2080), Gl. laevigata HK. (2059), Lygodium flexuosum SW. (2076), L. scandens SW. (2077), Lycopodium cernuum L. (2078), are numerous. In a further stage brushwood develops with Melastoma, Breynia, Ficus hirsuta VAHL, Rhodomyrtus tomentosa WIGHT, etc. Some scattered big trees of Schima bancana MIQ. (2081) are purposely left standing from the original vegetation.

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[1]) VAN STEENIS (1935), p. 177—180.

[2]) Padang is the Malay name for plain.

[3]) HARDON, Padang soil, an example of podsol in the Tropical Lowlands, These Proceedings, p. 530. This article will be published shortly in the "Natuurkundig Tijdschrift voor Ned.-Indië".

[4]) These are the numbers of my collection; most of them are in the Buitenzorg herbarium.

The secundary forest, which appears afterwards, when left to itself, will procure the cover of shade in which the true forest trees can germinate and develop, so that gradually the primary forest vegetation can be restored. This is, however, hardly the case here; in regard to the use of the land the country may already be called rather overpopulated, though the density of population is low. The kampong Sekolah darat between Melak and the Padang Loewai therefore was split up a couple of years ago, because all older forest in the neighbourhood had been cut down and the secundary forest had to be left to itself for many years to give the soil its necessary rest. In this secundary forest the following plants can be mentioned: Schima bancana MIQ. (2081), Homalanthus populneus O. K. (2130), Trema orientalis BL. (2131), Commersonia Bartramia MERR. (2132), Eugenia lineata DUTHIE (2133), Glochidion rubrum BL. (2134), Ficus hirsuta VAHL (2135), Rhodomyrtus tomentosa WIGHT (2121), Ormosia bancana PRAIN (2120), Daphniphyllum laurinum BAILL. (2140), Anisophyllaea disticha BAILL. (2191). The small rivers flow through rather broad valleys, 10—20 meter below the level of the terrace; they are mostly rather broad, with a flat swampy bottom. The ferns found here are characteristic for such localities: Dryopteris prolifera C. CHR. (2105), Dr. gongylodes O. K. (2104), Asplenium longissimum BL. (2107), Nephrolepis radicans KUHN (2106), Helminthostachys zeylanica HK. (2096).

These few details regard the route from Melak to the village Sekolah darat. From this place to the Padang Loewai the landscape is at first of the same kind, until the primary forest is reached.

Here the soil, which along the route is sandy, but usually grey coloured, becomes lighter, more yellowish. The fields, according to our Dayaks guides, become poorer and the forest further on the way towards the real padang has not been cut down, because the soil is considered by the population to be too infertile and thence not worth while. This was expressely stated.

The primary forest here is of another type than the primeval forest, which can be used for cultivation after cutting down and burning. Instead of consisting of huge trees intermixed with lower ones and with undergrowth, this forest is much lower, and consists, except a scanty developed undergrowth, of trees of one size only. On the soil mosses occur, which form at first a thin layer equally distributed. More into the interior the layer becomes thicker and more concentrated towards the base of the trees. The forest becomes lighter, the trees shorter; the distances between the trees become gradually larger, or better, the trees are now not evenly distributed, but more or less segregated into groups, with open places between. These open places become larger and may ultimately fuse together, so that the forest becomes a more or less open landscape with scattered groups of small trees, which groups may be sometimes more or less connected. In the open places the mossy layer, which is of considerable thickness below the trees, becomes thinner, and ultimately may disappear;

than only a thin layer of Lichens, much resembling Cladonia, is present, which may be broken up, so that the white sand comes bare. Under the trees, below the moss, a layer of loose peat, mostly 5—15 cM thick, is found.

Thus there is a gradual transition from a typical tropical rain forest to the typical padang-flora: an open landscape with groups of trees, which landscape resembles some types of the heather vegetation, as found e.g. on the high sandy soils of Gelderland and Utrecht [1]). As will be discussed afterwards this resemblance is not an accidental one only.

The study of the elements of the vegetation was handicapped by the circumstance that our visit was a short one only and that many plants did not flower at that time. The following details can be mentioned.

In the transitional forest the most common trees are Tristania obovata R. Br. (2182) and Vaccinium bancanum Miq. (2148) with some Podocarpus neriifolia Don (2188)

The bushes, because they are richer in species, give a more varied appearance. Vaccinium bancanum Miq. (2148) is most frequent here also, with Tristania obovata R. Br. (2182), but other elements are Eugenia spicata Lamk (2164), Cratoxylon glaucum Korth. (2210), and C. ligustrinum Bl. (2229); less frequent are Glochidion rubrum Bl. (2209), Arthrophyllum diversifolium Bl. (2163), Rhodomyrtus tomentosa Wight (2178), Rapanaea species (2215), Dacrydium elatum Wall. (2175), Daphniphyllum laurinum Baill. (2213), Choriophyllum malayanum Bth. and in one place Ixora cf. linggensis Brem. (2166). Because of the open character crown epiphytes are frequent; they do not occur only on the trees, but also on the soil. Here may be named Cyclophorus lanceolatus Alston (2183), Drynaria sparsisora Moore (2174), Davallia denticulata Mett. (2180), Humata species (2147); further Dischidia Rafflesiana Wall (2149); Myrmecodia Spec. and Hydnophytum Spec. Ants are frequent, as shown by the occurrence of Dischidia, Myrmecodia and Hydnophytum, but they occur also in nests on the branches, especially of Cratoxylon glaucum Korth. The parasite Henslowia buxifolia Bl. (2159) is also frequent and causes much havoc in the crowns of the trees.

The number of Orchids is considerable too; species of Dendrobium, Thrixspermum and Grammatophyllum (anggrek teboe) were observed; they have not been named yet. Nepenthes Reinwardtiana Miq. (2146) is also rather common in the shade of the bushes.

In the open places but a few species are found; except the Cladonialike lichens, Xyris complanata R. Br. (2162), which is conspicuous by its yellow flowers is found here with Schizaea dichotoma Sw. (2185). In

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[1]) In the same way as mentioned for the flora of Mandor (Polak (1933), p. 24; Schuitemaker (1936), fig. 11); the vegetation there is, at least locally, not so specialised, as shown by the occurrence of Gleichenia linearis Clarke, Pteridium aquilinum Kuhn, and Lycopodium cernuum L.

one place near the margin of the area further Dianella species (2165), Nephrolepis hirsutula PR. (2216) and Digitaria longiflora PERS. (2179) were found. This short sketch may suffice to give an idea of the character of this vegetation.

If we analyse the components, we see that the epiphytes are common ones, which, because their growth is influenced by conditions of light and humidity only, are also found on suitable places, as crown epiphytes, in the surroundings. This holds true both for the ferns and for the antplants; the latter are usually frequent in open forest, e.g. on tree-groups, which may be found on mountains slopes, regularly grazed by cattle.

For the other plants, however, there is no doubt that here too the peculiar character of the vegetation is due to edaphic conditions, as has been shown already by former authors on this subject for other localities and which is evident at once if we study the data given by HARDON on the samples from the Padang Loewai.

The plants, except the epiphytes, mentioned above must be able to live on soil of high acidity and poor in mineral plant food. Of this type are in the open places: the herbs Schizaea dichotoma SW. and Xyris complanata R. BR. and of the trees and bushes: Vaccinium bancanum MIQ., Cratoxylon glaucum KORTH. C. ligustrinum BL., Dacrydium elatum WALL. Eugenia spicata LAM., Tristania obovata R. BR. Rapanaea species; further Rhodomyrtus tomentosa WIGHT, Ixora, Daphniphyllum laurinum HK., Nephrolepis hirsutula PR. and Digitaria longiflora PERS., which may also occur in the bloekar, on more fertile soil of this type. Pteridium aquilinum KUNTH. which is very frequent elsewhere, was not found here.

When we study the localities of these plants on Java, we see that, of a number of those mentioned above, either the same species or other species of the same genus, are typical mountain plants. Vaccinium bancanum MIQ. does not occur on Java below 1500 M. From the genus Rapanea the Java species R. avenis MEZ occurs there from 1400—3000 M., and R. Hasseltii MEZ from 2700—3000 M. Podocarpus neriifolia DON occurs on Java usually above 1000 M., but rarely descending to 400 M. Dacrydium elatum WALLICH occurs on Celebes and N. Sumatra between 900—3000 M.

In other similar vegetations plants of the same type have been found e.g. Leptospermum flavescens SM. [1]) which occurs on Java between 1700 and 3300 M. and Styphelia malayana J. J. SM. [2]) (Styphelia pungens KDS is found on Java between 2100 and 3300 M.).

Herein is an analogy to the solfatara flora, in which it was observed, that alpine mountains plants may be found 1000—1500 M. below their usual altitude. VON FABER [3]) gives as explanation that the climate has no direct influence, but that in both localities, the alpine region and the

[1]) VAN STEENIS (1933), p. 38.
[2]) VAN STEENIS (1932), p. 182.
[3]) VON FABER (1927), p. 65, 69; VON FABER—SCHIMPER (1935), p. 552, 1294.

solfatara's, the soil is of a high acidity and poor in mineral plant food and in nitrogenous matter. In such vegetations Ericaceae play the first role and also epiphytes of the surrounding forests may penetrate into it. Though many details remain to be observed, we may explain the occurrence in this padang flora of plants, known elswhere as mountains plants only, on the same grounds.

That the peculiar character of the flora of the Padang Loewai on the flat watershed is due to edaphic factors becomes also clear by a comparison with the flora on the valley slope of the Soengei Loewai. N. of the Padang. As soon as the surface slopes down to the river, which is situated about 20 M. below the Padang, the vegetation becames at once more abundant; the common forest of large trees, intermixed with smaller ones and of undergrowth, though not a dense one, so characteristic for this type of forest, appears. From the plants collected may be named Nepenthes gracilis KRTH. (2192), Trichomanes singaporianum V. A. v. R. (2194), Cyathea brunonis WALL. (2196), Alsophila commutata METT. (2200), Syngramma quinata CARR. (2197), S. alismaefolia J. SM., var. Wallichii (2198), Elaphoglossum melanostictum MOORE (2204), Barclaya Motleyi HK. (2202) (in the river), which show at once that here again occurs the type of forest of the Sunda land at low altitude, with many elements, which do not occur on Java or have been found there but rarely in its W. part only. The soil on the slopes is not leached out yet so far, though it is not a rich soil; the water in the river is brown coloured by humic acid.

Because this type of vegetation, except in the last few years, has been relatively rarely discussed in botanical literature, it might be supposed that it is but rarely found. There is reason to believe, however, that it is of a rather widespread occurrence in the Outer Possessions of the Netherlands East Indies, especially on Sumatra, Borneo and the neighbouring islands on the Sunda-shelf and also on New Guinea in places with an old soil often built up of material, poor in plant-food, and not rejuvenated by recent volcanic action, where a climate with abundant rainfall with no well marked dry season occurs. The fact that these regions are at least until at present, not suitable for intensive agriculture and for European estates, may explain that relatively few details have been described about them, except in the last few years. The leaching out, though not so intensive as in the highly podsolised soil of the Padang Loewai already went rather far in big surfaces of the Outer Possessions, especially in E. Sumatra, Banka, Borneo and N. New Guinea; in this regions the soil is rather poor and can sustain but a scattered population, by shifting cultivation only. Ironwood (Eusideroxylon Schwageri T. et B.) is typical for this type of soil. Only in few cases such poor soils can be used for more intensive cultivation (e.g. for pepper), but in that case it needs high manuring, in the same way as the diluvial sandy soil of the

Netherlands had to be improved by compost or artificial manure. The good physical conditions of these soils is than an advantage.

Analogous vegetations, dependent on the leaching, and perhaps even podsolisation of the soil, are found also in other parts of the tropics, at low altitudes, in regions with no recent volcanic action and a large, evenly distributed rainfall. Their occurrence in other parts of Dutch Borneo and in British Borneo [1]) is hardly surprising. From the data of the literature the savanna's near the coast in Surinam were already by IJZERMAN [1]) and VAN STEENIS [2]) considered to be of the same type. The sketch given recently by LANJOUW [3]), confirms this. This type of forest, and that described by RICHARDS [4]) from British Borneo is not so extreme as that of the Padang Loewai. The upland savanna's may be influenced by different factors.

The agricultural value of the leached soils, described from Surinam by STAHEL and MULLER, may be about the same as the Borneo soils in the neighbourhood of the Padang Loewai, mentioned above.

I agree with VAN STEENIS in considering this and similar padang flora, e.g. of Mandor, as original ones. When sometimes, and usually in more fertile parts, the vegetation is influenced by men, especially by burning, Pteridium, Gleichenia, Nephrolepis and Lycopodium are mentioned; these plants are also typical for newly left ladangs on unfertile soils.

The formation of this peculiar vegetation is possible only on elevated well drained localities in a humid climate, with the rains equally distributed over the year, so that the soil is continuously leached and no ascending ground water, which transports mineral substance to the surface, can occur. These conditions are essentially the same as for the poor heather vegetation in higher places in Holland.

I do not agree with LANJOUW on his interpretation of the Surinam-savanna. He ascribes the xeromophic appearance of the flora to the influence of the dry season and the leaching of the soil to the heavy rains during the wet season. The padang-vegetation of Borneo proves, once more, that xeromophic structure is not necessarily an indication of a dry climate; it is neither in the mangrove vegetation [5]). Moreover, leaching is not so much dependent on heavy rainfall in one season, but more by a rather continuous rainfall throughout the year, which needs not to be very heavy. In the Dutch East Indies some parts e.g. the Western slope of the Mt. Moeria (the stations Petjangaan and Keling) and the country near

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[1]) WINKLER (1914), p. 202, pl. 4; RICHARDS (1936), p. 23—25, pl. 3, fig. 4; this type of forest is not so extreme.

[2]) VAN STEENIS (1932), p. 186.

[3]) LANJOUW (1936), *a*, p. 405; (1936), *c*, p. 826—846; see also EMANUELS (1936), p. 118.

[4]) RICHARDS (1936), p. 23—25.

[5]) The typical plants of the high moor flora are also xeromorphic; see VON FABER—SCHIMPER (1935), p. 1164.

Macassar in S.W. Celebes have very heavy rains during the wet season, and a well marked dry season, with ascending ground water.

If we distinguish with MOHR [1]) the months with a rainfall higher than 100 mM. as wet months, and with less than 65 mM. as dry months, we see, as shown in the following tables, that the type of rainfall both in Paramaribo and Republiek resembles that of Melak near the Padang Loewai in having no dry months; ten months of the year are in the Surinam localities wet months. The maximum monthly rainfall in both places in Surinam does not exceed 300 mM. In Macassar, Petjangaan and Keling, however, there are 4 dry months and only 6.6 and 7 wet months, but with a heavy rainfall, to about 700—900 mM.; this maximum is about three times as much as in Surinam! In such regions we can find a monsoon forest, which, as WINKLER pointed out already, is quite different; also the savanna's which develop there after cutting and burning. The soil has a high pH, may be even slightly alkaline and usually contains sufficient mineral plant-

Rainfall of the localities mentioned.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	total.	number wet months	number dry months
Melak	332	271	259	370	332	246	116	144	152	227	354	353	3156	12	0
Parimaribo	255	170	204	288	298	280	209	154	72	71	135	223	2159	10	0
Republiek	172	118	144	226	291	290	215	154	77	64	107	210	2069	10	0
Macassar	688	541	426	158	89	70	34	10	13	42	174	611	2856	6	4
Petjangaan	697	537	440	175	95	46	44	35	39	105	213	502	2928	6	4
Keling	871	707	476	201	124	74	22	19	35	61	149	513	3252	7	4

food, though the structure is often rather bad to bad; sandy soils of the Padang type have not been found.

Moreover it may be remarked here that coriaceous leaves as in the Ericaceae are scarce in the vegetation of savanna's in regions with a strongly marked dry season; most of the trees are thorny and drop their herbaceous leaves during the dry season.

Leguminosae, often in symbiosis with bacteria, are frequent in these dry savanna's, instead of Coniferae and Ericaceae with mycorhiza, characteristic for acid soils in a humid climate as in the Padang Loewai.

We thus see that this acid soil enables a number of plants, which otherwise occur on the mountains of Malaysia, and which are not stenotherm, to descend here in the lowlands, even nearly to sea-level. In these respects this flora resembles that of the solfatara's. Podsolised soils, as found on the Padang Loewai may be of more widespread occurrence in the tropics,

[1]) MOHR (1933), p. 100.

than hitherto supposed but in the economically less developed and therefore not intensively studied regions.

Finally I wish to express my sincere thanks to Ir. H. WITKAMP for his great hospitality during my stay in Koetai and to Dr. C. G. G. J. VAN STEENIS who made most of the identifications.

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Geophysics. — *On a Period of 27 Months in the Rainfall.* By S. W. VISSER. (Communicated by Prof. E. VAN EVERDINGEN).

(Communicated at the meeting of May 29, 1937.)

A research into the possibility of long range weather forecasting in the Netherlands led to the investigation of a period of 27 months in the weather of different regions. We found clear indications of this period in Eastern America, on Iceland and in Western Europe. It shows close connections with the warm currents of the North Atlantic Ocean.

The data, upon which the following considerations have been based, were taken from "World Weather Records"[1]) and different publications of De Bilt[2]). We have restricted ourselves in this paper to the rainfall. The process applied was as follows. In the first place seasonal totals of rainfall were calculated from the available data, then averages and the deviations therefrom were deduced. These deviations were arranged in nine columns, representing the whole period of 27 months, and the average values representing the character of the oscillation were determined.

The curves obtained are generally very complicated and we have surely not to do with a simple phenomenon. Fig. 1 represents the features of the period for four stations. In Western Europe it is characterized by a well

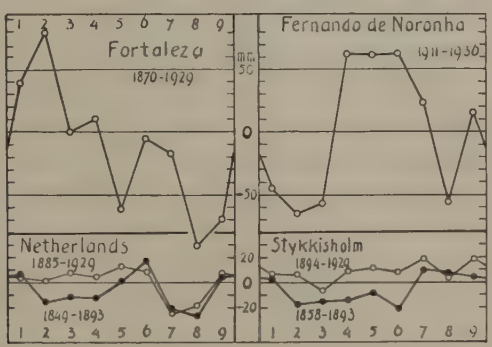

Fig. 1.

developed minimum during the 7th and the 8th season of the period, as is obvious in the curve of the Netherlands. We state very high amplitudes at Fortaleza (Ceara, Brazil) and on Fernando de Noronha. As a rule the

[1]) World Weather Records, Smiths. Misc. Coll. **79**, 1927; **90**, 1934.

[2]) C. BRAAK, The climate of the Netherlands, Precipitation. Meded. en Verh. **34** *a*; C. BRAAK, The climate of the Netherlands West Indies, Meded. en Verh. **36**; Annuaires Inst. royal des P.B.; Maandel. Overzichten der Weersgesteldheid in Nederland; Overzichten Met. Waarn. in Ned. West-Indië.

stability is remarkably good, as appears when comparing the curves for two parts of the interval investigated (Netherlands and Stykkisholm). Even during cycles of nine years duration, containing four periods of 27 months, the stability in the precipitation in the Netherlands is fairly constant (Table 1).

TABLE I. Stability of 27-Month Period in the Rainfall of the Netherlands.

	1	2	3	4	5	6	7	8	9
1849—1857	— 2.2	—18.7	—20.9	—12.9	—22.7	— 2.7	+39.8	—49.3	—26.7
1858—1866	—16.6	—23.9	—17.2	—32.0	—35.6	+ 4.9	—22.6	— 4.4	+ 0.9
1867—1875	+39.2	—32.3	+22.2	—34.4	— 2.2	+30.9	—43.0	—28.3	+23.3
1876—1884	+28.8	+24.1	— 2.5	+16.0	+41.0	+26.0	—15.4	—18.7	+ 2.2
1885—1893	— 3.7	—26.5	— 4.5	+ 0.3	+22.4	+25.8	—64.7	—32 2	+18.5
1894—1902	—24.4	—35.6	+48.9	—18.5	—19.8	+ 1.1	+ 3.8	— 9.7	— 7.6
1903—1911	— 4.5	+37.2	+19.6	+37.7	+ 3.0	—38.7	—47.2	—36.2	+13.0
1912—1920	+36.0	+ 0.0	+15.2	+28 3	+19.9	+37.2	— 2.2	+ 3.4	—28.8
1921—1929	— 9.3	+ 5.4	+ 6.0	—35.3	+ 9.5	— 5.8	—23.2	—16.1	+41.2

The severest exception is that of the cycle 1894—1902. About the end of the century an important change in the weather elements of Europe has been stated [3]) and this fact influences evidently the character of the period.

It seemed worth while to investigate the character of this period on and round about the Northern Atlantic Ocean. Though it is open to question, whether we may apply harmonic analysis, we have done so in order to detect some general features of this period. The calculations have been restricted to the first two terms of the series.

For most of the stations investigated the rainfall between 1876 and 1929, being 54 years or 6 nine-years cycles, has been studied. The successive cycles started, with the winters of 1876 (December 1st, 1875), 1885 etc. (See Table 1). The present period of 27 months started with the autumn of 1936.

We found in the first place that we could subdivide the stations in two groups, 1°, a group with its maximum about the 5th to the 7th month: Fortaleza and Charleston in America and a number of stations in Europe: the Netherlands, Great Britain, Oslo, Breslau and Paris; 2°, a group with its maximum during the 14th month or later, Fernando de Noronha, Barbàdos, Bermuda, Stykkisholm, Thorshavn (Faroer).

The first group contains continental stations, the other group principally oceanic ones. Therefore we may presume an action at sea differing greatly

[3]) A. SCHMAUSS, Beitr. z. Phys. d. fr. Atm. **14**, 1932.

from that on land. Even at relatively small distances the character differs considerably: Fernando de Noronha and Fortaleza, Aberdeen and Thorshavn, Oslo and Bodö (See Table 4).

The second feature revealed is a retardation combined with a decrease of the amplitude on the Atlantic Ocean in the direction of the Gulfstream, as shown by the following harmonic formulae.

TABLE 2. Harmonic Analysis of 27-Month Period on the Atlantic Ocean.

						Maximum
F. de Noronha	3.8° S 33.5° W	53.9 sin (x + 265.3°) + 40.9 sin (2x + 146.5°)				13.8 month
Barbados	13.1 N 59.6 W	13.2	262.1	8.9	108.0	14.1
Bermuda	32.3 N 64.8 W	24.1	226.1	13.7	120.1	16.8
Ponta Delgada	37.7 N 25.7 W	2.2	209.6	8.5	206.6	18.0
Stykkisholm	65.5 N 22.8 W	8.6	187.2	0.4	204.8	19.7
Thorshavn	62.0 N 6.8 W	9.0	158.1	7.3	68.3	21.9
Bodö	67.3 N 14.4 E	15.1	184.9	11.5	281.2	19.9

N.B. Fernando de Noronha 1911—1936; Barbados 1883—1930; Thorshavn 1873—1925.

The large amplitude on Fernando de Noronha shows that probably here or in the neighbourhood the disturbance takes its origin and the table teaches that the wave needs six or seven months to cross the Ocean; it depends probably on changes in the Gulfstream under the influence of the trade winds or other meteorological factors. This result corresponds with that of GALLÉ [4]), who deduced high correlation coefficients between the trade winds in the summer and the following winter temperatures in Europe.

The rainfall minimum in Western Europe coincides strictly with the arrival of the maximum in the NE Atlantic. Harmonic analysis yields the following results,

TABLE 3. Harmonic Analysis of 27-Month Period in Western Europe.

						Minimum
Greenwich	51.5° N 0.0°	11.8 sin (x + 357.4°) + 10.8 sin (2x + 130.4°)				20.4 month
Netherlands	52 N 5 E	11.2	358.4	12.6	133.8	20.4
Paris	48.8 N 2.5 E	9.1	350.8	8.1	128.3	20.9
Aberdeen	57.2 N 2.1 W	6.6	346.4	12.2	114.0	21.3
Breslau	51.1 N 17.0 E	3.3	354.4	9.4	92.3	20.7

[4]) P. H. GALLÉ, Verslagen K. Ak. v. Wet. Amsterdam, 27 Febr. 1915, 29 Jan. 1916; Proc. Royal Acad. Amsterdam, **17**, 1147 (1915); **18**, 1435 (1916).

The importance of these results for the long range weather forecasting in Western Europe is evident. The superfluous rain in the fifth season on Fernando de Noronha is followed by deficient precipitation in the seventh season in Western Europe. The dryness of the seventh season is best developed at Greenwich. Out of 24 periods, 1876—1929, 19 were here too dry. We have a probability of 80 % when forecasting a too dry seventh season at Greenwich. In the Netherlands 18 seventh seasons during the same time interval were too dry and during the 36 periods, 1849—1929, 26 cases (72 %) gave a deficient precipitation. These figures are foreshadowing a too low rainfall during the coming seventh season: the spring of 1938.

Comparison with the rainfall on Fernando de Noronha is only possible since 1911. The connection between the precipitation for 11 periods, 1911—1936[5]), during the fifth season on this island and that during the seventh season in the Netherlands is shown in fig. 2. The abscissae procure the deviations of the seasonal averages of Fernando de Noronha, the ordinates those of the Netherlands. The figures refer to the dutch seasons (W winter, L spring, Z summer, H autumn). The contrast is present, but important exceptions exist. Especially we point to the large discrepancies of two seasons, the summer of 1931 and the autumn of 1915.

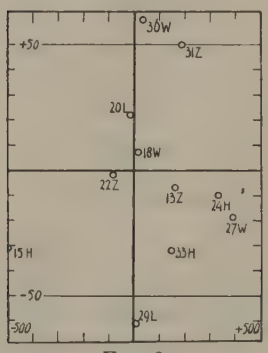

Fig. 2.

We may be sure that the weather in Western Europe does not depend upon the Gulfstream only and other factors doubtless disturb the regular development of the Gulfstream activity.

Moreover the harmonic analysis does not yield trustworthy results, when other actions are present also. So the small irregularities in the months of arrival of the maximum at Thorshavn and Bodö are due to failure of the harmonic analysis. When consulting the original figures we see that the wave arrives at the Faroer at an earlier date, about the 20th month, at Bodö, however, later, about the 21st month (see table 4).

The contrast between the rainfall maximum at sea and the simultaneous minimum on land appears to be a general rule and the figures point clearly to a retardation of the minimum along the eastern coasts of America, everywhere coinciding with the passing of the maximum on the Atlantic. We state exceptions to be present in the NE of North America, at Toronto and Eastport and at Ivigtut on Greenland, evidently being situated outside the area of activity of the Gulfstream.

Table 4 gives the averages of the continental and oceanic stations investigated.

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[5]) Boletim Mensal and Boletim Diario, Dir. Met. Rio de Janeiro.

TABLE 4. 27-Month Period. Average Values for Nine Seasons. Rainfall in mm.

	Oceanic Stations									Max. month
	1	2	3	4	5	6	7	8	9	
F. d. Noronha	−45	−65	−58	**+62**	**+61**	**+62**	+23	−56	+15	14
Barbados	+10	− 2	−30	**+28**	− 2	**+28**	+10	0	−33	14
Bermuda	+15	−33	−41	− 8	**+33**	+ 8	+15	+23	−30	17
P. Delgada	−10	−10	0	+ 4	+ 8	− 1	−10	+10	+ 9	18
Stykkisholm	+ 2	− 3	− 5	− 2	0	− 3	**+ 6**	+ 2	+ 4	20
Thorshavn	+ 4	+11	− 6	−30	− 1	**+20**	**−12**	**+17**	− 5	20
Bodö	−15	− 3	−13	0	−22	+ 4	**+20**	**+26**	+ 3	21
	NE America									
Toronto	−21	+19	+ 4	+ 8	−14	+14	− 2	− 7	0	—
Eastport	− 6	+18	−23	+13	− 3	+20	+13	− 5	−18	—
Ivigtut	−20	−32	− 3	+ 9	+27	−16	+12	+33	−11	—

	Continental Stations									Min. month
	1	2	3	4	5	6	7	8	9	
Fortaleza	+39	+79	0	+10	**−60**	− 5	−17	−90	−70	14
Paramaribo	− 3	− 5	− 2	−27	+ 7	**−18**	+21	+19	+ 7	14
Key West	+20	−27	−18	+20	+36	− **6**	**−10**	− 5	−11	17
Charleston	− 1	+ 5	+13	+37	−13	−17	**−28**	− 7	−22	17
Valentia	+10	+22	− 7	+ 4	− 2	+ 3	**−14**	− 2	−15	19
Greenwich	+ 5	+ 3	+ 3	+11	+11	+ 6	**−24**	−15	− 1	20
Aberdeen	+14	− 5	+ 4	− 2	+11	+11	**−14**	−17	− 2	20
Netherlands	+ 4	+ 1	+ 7	+ 5	+13	+ 8	**−25**	−18	+ 6	20
Paris	− 4	+ 8	+ 6	− 2	+17	+ 7	**−26**	− 5	− 1	20
Oslo	+17	−14	+ 2	− 8	+ 6	+11	+10	**−18**	− 7	22
Breslau	+14	− 3	+ 1	− 8	+16	− 1	− 3	**−14**	− 2	22

Biochemistry. — *The splitting off of gallic acid from tannin, especially from theotannin, by Aspergillus niger.* By W. B. DEYS and M. J. DIJKMAN. (Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of May 29, 1937.)

Various researches [1]) have proved that tea-tannin belongs to the group of the catechins.

Only a few researchers have found that gallic acid can be split off from theotannin by means of hydrolysis even as from gallo-tannin. TRETZEL [2]) mentions that gallic acid can be obtained by boiling tea-tannin with sulphuric acid.

From the researches of TSUJIMURA [3]) follows that tea-tannin is the gallic acid ester of tea-catechin; tea-tannin splits off gallic acid when hydrolysed with diluted sulphuric acid. According to TSUJIMURA this hydrolysis is to be formulated as follows:

$$\underset{\text{tea-tannin}}{C_{22}H_{18}O_{10}} + H_2O \rightarrow \underset{\text{tea-catechin}}{C_{15}H_{14}O_6} + \underset{\text{gallic acid}}{C_7H_6O_5}$$

Other researchers [4]) do not mention the fact that gallic acid can be obtained from tea-tannin by hydrolysis in some way or other.

It has been known for a long time past that the fungus Aspergillus niger is able to split off gallic acid from gallo-tannin. Therefore it was the obvious thing to do to investigate the behaviour of tea-tannin with respect to A. niger. To this end we made the following experiments:

1. A. niger was inoculated on a decoction of fresh tea leaves.
2. We inoculated the fungus on a solution containing saccharose, a definite concentration of nutritive salts and theotannin.
3. The enzyme of A. niger was isolated and put into a solution of theotannin in water.

In each of the three experiments the liquids were examined on gallic acid after three days. From the undermentioned results it was evident that in each of the three cases gallic acid could be isolated. Although it

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[1]) See SHAW and JONES, Theotannin p. 74—95, Madras 1932.

[2]) TRETZEL cit. NANNINGA, Reports from 's Lands Plantentuin (the Botanical Garden at Buitenzorg) N°. XLVI.

[3]) TSUJIMURA, Sci. Papers Inst. of Phys. and Chem. Research. Tokyo, Vol. **14**, p. 63 (1930) and Vol. **15**, p. 155 (1931).

[4]) YAMMAMOTO, J. Agric. Soc. Japan, **6**, 564 (1930); DEUSS, Reports from the Experimental Station for Tea, XLII, 1915.

may very well be possible that tea contains more than one sort of tannin, we may conclude from our researches that at least one of these tannins is a gallic acid ester.

EXPERIMENTAL PART.

1. *Isolation of Aspergillus niger.*

There are various methods to isolate A. niger. The most simple one is the method in which we make use of the ability of this fungus to split off gallic acid from tannin solutions by means of its specific enzyme, the tannase. Making use of this property A. niger can easily be isolated by pouring a fairly concentrated tannin solution on any substrate (for instance garden's soil). After a few days the growth of the mycelium and the development of the conidiae-bearers of A. niger on the liquid are perceptible. By inoculating the conidiae on one of the well-known nutrient media for fungi one can easily get a pure culture of this fungus in a few days.

For the following experiments the matrix used for the isolation consisted of ordinary earth taken from between the tea-shrubs in the experimental garden of the Experimental Station.

By spreading a small amount of this earth on a petri dish and pouring a 5 % tannin solution on it we could as early as three days later proceed to the inoculation of pure cultures. The spores which had been formed were inoculated on nutrient agar. Microscopical examination showed that the inoculation thus obtained was a pure culture of A. niger.

2. *Colorimetric determination of gallic acid.*

A solution containing 10 grammes of potassium ferricyanide and 100 ml ammonia (25 %) per liter turns dark red when added to a solution of gallic acid and proved to be very suitable for a colorimetric determination of gallic acid.

In order to be able to see whether a tannin solution contains gallic acid it was necessary first to precipitate the tannin by means of gelatine. The addition of 10 ml of gelatine solution (25 g gelatine on 875 ml water) and 5 g kaolin proved sufficient for 5 ml 5 % tannin. After 45 minutes' shaking the filtrate was free from tannin. The amount of gallic acid in the filtrate was ascertained colorimetrically by means of the above mentioned method.

3. *Hydrolysis of gallo-tannin by A. niger.*

Firstly we traced how much free gallic acid a 5 % solution of commercial tannin contained. By means of the above mentioned method we found that there was less than 5 mg gallic acid in the solution (this is less than 0.5 %). Further we ascertained how much gallic acid was split off by

A. niger from a 5 % tannin solution which also contained per liter 25 g ammonium sulphate, 0.75 g dipotassium phosphate, 0.25 g magnesium sulphate and a trace of zinc sulphate. On this solution we inoculated a culture of A. niger. After three days the filtrate was examined on gallic acid. There appeared to be 2.0 % free gallic acid in the solution. This is about the solubility of gallic acid at the temperature of the experiment (27 to 28° C).

We also tested whether spores of A. niger grow on the above mentioned salts and 5 % tannin solution and whether here too the splitting off of gallic acid could be proved. As early as one day later the growth of the fungus was clearly perceptible, after three days the actual presence of free gallic acid was proved by the colorimetric method.

The original solution which contained less than 0.5 % gallic acid proved to contain 2.2 % gallic acid after the experiment.

4. *Gallic acid liberated by A. niger from a decoction of tea leaves.*

100 grammes of fresh tea leaves (p + 2) were boiled with 250 ml distilled water during 30 minutes. Immediately afterwards the hot extract was filtrated from the infused leaves. When the liquid had cooled down it was extracted with ether in a STEUDEL-apparatus during two hours in order to remove the free gallic acid which might be present in the decoction [1]).

After the ether had been distilled we ascertained whether there was any gallic acid in the remaining liquid. To this purpose some theotannin which had also been dissolved in the ether had first to be removed by means of gelatine, after this a slight colour-reaction with soda indicated a trace of free gallic acid. It was impossible to isolate crystals of this acid.

The liquid which had been extracted with ether was placed in a water-bath of 50° C; meanwhile the last traces of ether were driven from the solution by means of a current of nitrogen. When the solution had cooled down to 30° C we inoculated it with spores of A. niger. After three days the gelatine-test proved that the fungus had decomposed all the theotannin. The liquid was filtrated from the mycelium and extracted with ether in a STEUDEL-apparatus during 12 hours. The etheric solution thus obtained was shaken with a saturated sodium bicarbonate solution; the bicarbonate solution was shaken three times with ether and finally acidified with diluted hydrochloric acid (10 %). The acid solution was extracted with ether, the etherial solution was dried on sodium sulphate and distilled.

The remainder proved to be a beautiful, more of less yellow substance crystallized in needles. On recrystallizing from water we obtained a colourless substance, which took a darker colour when heated to 220° C and

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[1]) DEUSS (Reports of the Experimental Station for Tea, XXVII, 1913) found that tea leaves contain a little free gallic acid. He had to work up several kilogrammes of dry tea leaves in order to obtain some decigrammes of gallic acid.

melted at 237° C with a pronounced development of gas. When mixed with pure gallic acid the melting point showed no depression. The colour reactions of this crystalline substance with ferric chloride, potassium cyanide, lime water, potassium plumbate and soda were equal to those of gallic acid.

We obtained 234 mg of crude substance of which, according to the colorimetric method, 220 mg proved to be pure gallic acid.

The ascertainment of molecular weights according to RAST gave the following figures:

0.288	0.663	0.376	mg substance in
7.701	10.960	7.056	mg camphor:
$\triangle$: 8.6	13.9	12.6° C.	

Calculated molecular weight for $C_7H_6O_5$ (gallic acid) : 170

Found : . . . . . 174, 174, 169.

5. *Preparation of theotannin.*

100 grammes of green tea leaves (p + 2) were boiled during 30 minutes with 250 ml distilled water. After cooling down the warm filtrate was shaken three times with benzol and after that three times with chloroform. By means of a nitrogen current the chloroform was removed from the watery solution, which was then extracted with ether during 12 hours. After distilling the ether we dissolved the treacly residue in 25 ml distilled water.

The precipitate that formed itself when neutral lead acetate was added in excess, was washed with water a few times. Then the leadsalt was removed by means of centrifuge and treated with hydrochloric acid (5 %), so that the lead chloride precipitated and the theotannin passed into the watery solution. This solution was filtrated from the lead chloride; the filtrate was extracted with ether.

The etherial solution was dried on sodium sulphate and the ether evaporated, after which the dry residue was dissolved in a small amount of pure ethyl acetate. When chloroform was added an amorphous white substance precipitated. This was filtrated and while still damp with chloroform it was once again dissolved in ethyl acetate and precipitated with chloroform. The precipitate was washed with chloroform until the filtrate left no solid substance when evaporated on a watch-glass.

When the precipitation with chloroform is done very carefully crystals may be formed on the sides of the flask.

The theotannin which was still very damp with chloroform was dried with the filter in a vacuum dissiccator over P_2O_5. In this way absolutely colourless theotannin can be prepared. This product is quite tenable under nitrogen, when all moisture is carefully excluded.

Reactions on theotannin and gallic acid.

	theotannin	gallic acid
gelatine solution	precipitate	no precipitate
limewater	purple	blue → red
soda and sodium bicarbonate	brownish red when exposed to air (tea colour)	green when exposed to air
ferric chloride	blue	blue

In order to ascertain whether the theotannin, thus prepared still contained free gallic acid we dissolved 80 mg in 5 ml water; 10 ml gelatine solution and 1 g kaolin were added. After shaking the mixture during 45 minutes it was filtrated. In no way was there any gallic acid to be traced in the filtrate.

6. *Decomposition of theotannin by A. niger.*

160 mg theotannin was dissolved in 5 ml of a solution, containing per liter 1.00 g ammonium sulphate, 0.08 g mono ammonium phosphate, 0.12 g potassium sulphate, 0.30 g magnesium sulphate and a trace of zinc sulphate.

After adding 0.1 g saccharose to this solution we inoculated it with spores of A. niger. After standing 3 × 24 hours at roomtemperature (± 28° C) a heavy mycelium proved to have grown, whereas the tannin had disappeared almost completely from the solution.

After filtrating the liquid from the mycelium we added an ample quantity of sodium bicarbonate to the solution. The liquid was shaken three times with ether and after that acidified and completely extracted with ether. After drying the etherial solution on sodium sulphate and evaporating the ether we obtained a yellow crystalline product (weight after drying 30 mg).

From the colorimetric determination we learned that it contained 25 mg pure gallic acid. As, theoretically, only 38.9 mg gallic acid can be expected from 160 mg theotannin, this result of 25 mg may be considered to be high, when the obvious loss during isolation is taken into account.

After recrystallizing the crude substance from water we obtained a colourless product, which melted at 239° C and of which the mixture with pure gallic acid showed no depression of the melting point.

7. *Hydrolysis of theotannin by the ferment of A. niger.*

The enzyme, needed for these tests was obtained from a culture of A. niger according to the directions of FREUDENBERG [1]). We added 25 mg of the enzyme, isolated from A. niger, to a solution of 100 mg theotannin in 5 ml distilled water. After having kept this mixture at roomtemperature

[1]) FREUDENBERG, Chemie der natürl. Gerbstoffe, Berlin 1920, p. 48.

(27 to 28° C) during two days, we extracted it with ether. The etherial solution was shaken with a solution of sodium bicarbonate.

The fraction of bicarbonate, which had been acidified with diluted hydrochloric acid, was once more extracted with ether. When the ether was evaporated fine gallic acid crystals remained.

8. *Stability of gallic acid under the action of the ferment of A. niger.*

A solution of 10 ml 1 % gallic acid, 10 ml saltsolution (see above) and 0.1 g saccharose was inoculated with spores of A. niger. After 5 × 24 hours a heavy mycelium had formed itself, whereas the titrimetric method gave no indication of a decrease in the content of gallic acid.

Summary.

Three different experiments proved that the enzyme of A. niger is able to split off gallic acid from theotannin:

a. A. niger was inoculated on a decoction of fresh tea leaves.

b. We inoculated A. niger on a solution, containing theotannin, saccharose and nutritive salts.

c. The enzyme, isolated from A. niger, was added to a solution of theotannin in water.

After some days we could isolate crystalline gallic acid from each of the three liquids. The gallic acid obtained in this way was identified by means of melting point, molecular weight and melting point of the mixture of the isolated substance with pure gallic acid. We found that gallic acid is not decomposed by the enzyme of A. niger.

Although it may very well be possible that there are different tannins in tea, the conclusion that at least one of these tannins is a gallic acid ester, may certainly be drawn from the present investigations.

Proefstation West-Java.

Buitenzorg, Maart 1937.

Botany. — *Sur la transpiration de quelques halophytes cultivées dans des milieux différents en comparaison avec celle de quelques non-halophytes.* Par M. J. ADRIANI. (Communicated by Prof. J. C. SCHOUTE.)

(Communicated at the meeting of May 29, 1937.)

1. *Introduction.*

En 1898 SCHIMPER (10) exposait sa conception — longtemps classique — des halophytes. Etant données les nombreuses analogies morphologiques et anatomiques présentées par les halophytes et les xérophytes succulentes, on doit considérer les halophytes comme des xérophytes. Les taux élevés en sels des sols où elles vivent rendraient difficile l'absorption de l'eau par les halophytes, pour lesquelles les sols salés seraient „physiologiquement secs"; la circulation de l'eau dans ces plantes et leur transpiration seraient de ce fait limitées.

Cette conception a été critiquée, notamment par VON FABER (5) et STOCKER (12, 13, 14) qui, dans leurs expériences sur la transpiration ont trouvé des valeurs élevées pour les halophytes; de plus il résultait des recherches de DUVAL-JOUVE (4), de CHERMEZON (3) et de VAN LANGENDONCK (8) que les caractères anatomiques des halophytes n'étaient pas xéromorphiques, de sorte qu'à partir de 1925 environ la théorie de SCHIMPER était généralement abandonnée.

Cependant, les objections précédentes sont à leur tour contestées. Les expériences de BRAUN-BLANQUET, BHARUCHA et MEIER (2) sur la transpiration comparée de quelques halophytes méditerranéennes et de quelques plantes xéromorphiques des dunes ont montré que les halophytes transpirent très peu. SCHRATZ (11) étudiant la transpiration des halophytes du littoral de la mer du Nord est arrivé à la même conclusion. Ces dernières publications me conduisent à faire connaître brièvement les résultats de quelques expériences faites sur ce sujet au laboratoire de physiologie végétable de l'université municipale d'Amsterdam en 1934.

2. *Dispositifs expérimentaires, méthode de mesure.*

Les halophytes étudiées (*Obione portulacoides, Salicornia herbacea* etc.) ont été cueillies au printemps à l'état de plantules généralement et, pour un certain nombre à l'état de jeunes plantes, dans leurs stations naturelles sur le littoral de la mer du Nord (Bergen op Zoom). Au jardin botanique je les cultivais dans une serre sur un sol sablonneux contenant des concentra-

tions d'eau de mer différentes [relation eau de mer: eau distillée = 1 : 0 (= 1 eau de mer); 1 : 1 (= ½ eau de mer); 1 : 2 (= ⅓ eau de mer); 1 : 3 (= ¼ eau de mer)]. Les mésophytes étudiées comparativement (*Lamium maculatum, Ajuga reptans, Erica Tetralix* etc.) ont été cueillies dans le jardin botanique de l'université.

Les mesures de la transpiration ne furent effectuées que lorsque les plantes se furent bien adaptées à leur nouveau milieu, vers la fin du mois de juillet et au mois d'août. De préférence j'ai choisi des jours clairs, sans nuages. Les halophytes étant sorties de la serre où elles étaient cultivées, leur transpiration fut déterminée en pesant avec la balance analytique des tiges ou des feuilles fraichement coupées, puis, en repesant les mêmes éléments après une exposition de deux minutes à l'air libre. C'est par la différence de poids qu'on est à même de mesurer la quantité d'eau transpirée. Pour la critique de cette méthode je renvoie au travail de PFLEIDERER (9).

Pratiquement on peut exprimer les résultats soit par la quantité d'eau transpirée par unité de surface ($T_{/s}$; T = transpiration en milligrammes pendant une minute, s = surface en dm^2 de la côté inférieure de la feuille), soit par la quantité d'eau transpirée par unité de poids frais ($T_{,}$ p. f.; T = transpiration en milligrammes pendant une minute; p. f. = poids frais en grammes).

Si l'on veut comparer la transpiration d'espèces mésophiles, l'unité adoptée (surface ou poids frais) a moins d'importance que lorsqu'il s'agit d'une comparaison entre mésophytes et halophytes, car, à poids égal ces dernières ont une surface plus faible en rapport avec un volume plus grand. Il en résulte que les valeurs de la transpiration calculées par unité du poids frais seront toujours trop basses pour les halophytes. Il parait donc préférable de calculer la transpiration en fonction de l'unité de surface. Mais il faut considérer par contre que la surface, mesurée au moyen d'un planimètre n'est pas la surface transpirante au sens propre du mot. Sans tenir compte de la cuticule, la surface transpirante se compose principalement des espaces intercellulaires, dont la fonction est réglée par les ouvertures stomatiques, en ce sens que, dans beaucoup de cas les stomates interviennent comme le „facteur limitant" de la transpiration [HARTSUYKER (6)]. Au point de vue écologique on préfère le calcul en fonction de l'unité de poids frais [WALTER (15), VAN LANGENDONCK (8)], puisque c'est seulement d'après cette méthode que l'intensité de la transpiration reflète l'écologie des stations. J'ai appliqué les deux méthodes pour calculer la transpiration ($T_{/s}$ et $T_{,}$ p.f.) dans tous les cas où il m'était possible de déterminer la surface au moyen d'un planimètre.

Si par les expériences il se trouve que la transpiration des halophytes est limitée comparée à celle d'autres plantes — que celle-ci soit calculée par unité de poids frais ou par unité de surface — on a le droit de conclure que les halophytes transpirent peu.

3. *La transpiration des halophytes cultivées dans des milieux différents.*

Il résulte des courbes 1 à 7, relatives à la transpiration de *Obione portulacoides* et de *Salicornia herbacea*, que la transpiration diminue lorsque

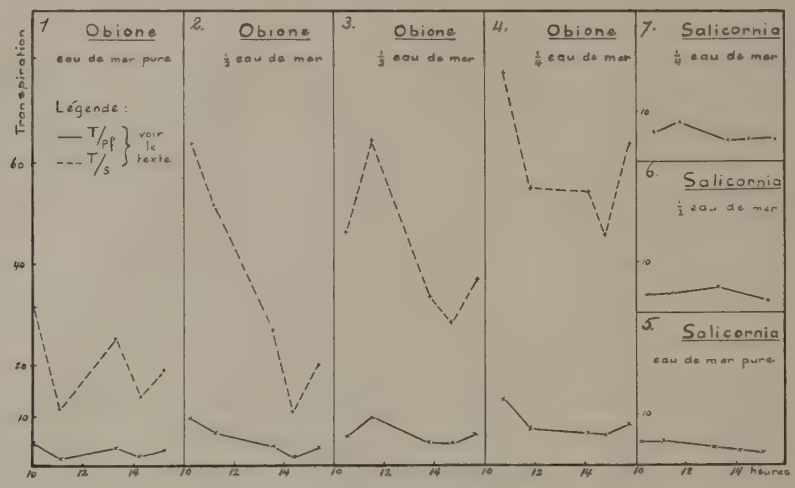

Fig. 1 à 4. Courbes journalières de la transpiration du 8 août 1934;
Fig. 5 à 7. Celles du 16 août 1934.

la concentration des sels s'élève dans la rhizosphère. [Comparer les résultats de KELLER (7)].

Valeurs moyennes de T/s pour *Obione*:		Egalement *Salicornia* T/p. f.:	
eau de mer pure . . .	19,9	eau de mer pure . . .	3,5
1/2 eau de mer	34,3	1/2 eau de mer	3,65
1/3 eau de mer	41,8	1/4 eau de mer	5,35
1/4 eau de mer	59,1		

Dans le cas de *Salicornia* les différences sont moins nettes; ceci s'explique sans doute par le fait que pendant les mesures le ciel était nuageux.

4. *La transpiration des halophytes comparée à celle de non-halophytes.*

Les valeurs moyennes résultant de toutes mes mesures de la transpiration sont réunies dans le tableau ci-dessous pour faciliter l'examen générale de toutes les données. On y trouve les valeurs de la transpiration en fonction de l'unité de poids frais et également celles en fonction de l'unité de surface.

J'ai ajouté encore les résultats des mesures de la transpiration chez quelques halophytes méditerranéennes, mesures faites par la même méthode dans la station naturelle de ces plantes au bord de l'étang de Pérols (près de Montpellier) en 1933 en collaboration avec H. MEIER (1). Les résultats peuvent être résumés ainsi : si l'on calcule la transpiration en fonction de

TABLEAU. Valeurs moyennes de la transpiration.

	Date	T/p.f.	T/s.
Saponaria officinalis	18—7—34	28.2	73.3
Comarum palustre	16—7—34	19.6	32.4
„ „	31—7—34	24.6	40.4
Valeriana officinalis	16—7—34	15.4	40.6
Ajuga reptans	18—7—34	9.62	34.6
„ „	31—7—34	15.3	50.—
Erica Tetralix	16—7—34	9.5	—
„ „	31—7—34	16.9	—
Calluna vulgaris	18—7—34	3.72	—
„ „	1—8—34	6 11	—
Arctostaphylos uva ursi	16—7—34	5.—	21.—
Plantes cultivées:			
Obione portulacoides (1)	31—7—34	3.31	29.8
„ „	8—8—34	2.64	19.9
Obione portulacoides (½)	1—8—34	4.23	31.7
„ „	8—8—34	5.—	34.3
Obione portulacoides (⅓)	31—7—34	6.63	50.2
„ „	8—8—34	6.04	41.8
Obione portulacoides (¼)	1—8—34	5.75	42.1
„ „	8—8—34	8.1	59.1
Salicornia herbacea (1)	16—8—34	3.5	—
Salicornia herbacea (½)	16—8—34	3.65	—
Salicornia herbacea (¼)	16—8—34	5.35	—
„ „	1—8—34	5.62	—
Plantes du littoral de la Méditerranée:			
Suaeda maritima	6—7—33	3.92	—
Juncus maritimus	6—7—33	3.78	—
Obione portulacoides	6—7—33	2 88	—
Salicornia radicans	6—7—33	2.51	—
Salicornia herbacea	6—7—33	2.32	—
Salicornia macrostachya (Arthrocnemum glaucum)	6—7—33	0.48	—

l'unité de poids frais, la transpiration des halophytes est limitée par comparaison avec celle des non-halophytes. Il apparait clairement qu'il en est de même si la transpiration est calculée en fonction de l'unité de surface. Donc : *les halophytes transpirent peu en comparaison avec les mésophytes.*

Mes conclusions rejoignent encore celles de BRAUN-BLANQUET et de SCHRATZ relativement à la circulation d'eau limitée chez les halophytes.

Les différences de transpiration entre halophytes et mésophytes qui ressortent si nettement à l'examen du tableau se vérifient aussi par les courbes journalières de la transpiration des différentes plantes (voir les courbes 8 à 17). Il en résulte également que la transpiration calculée en

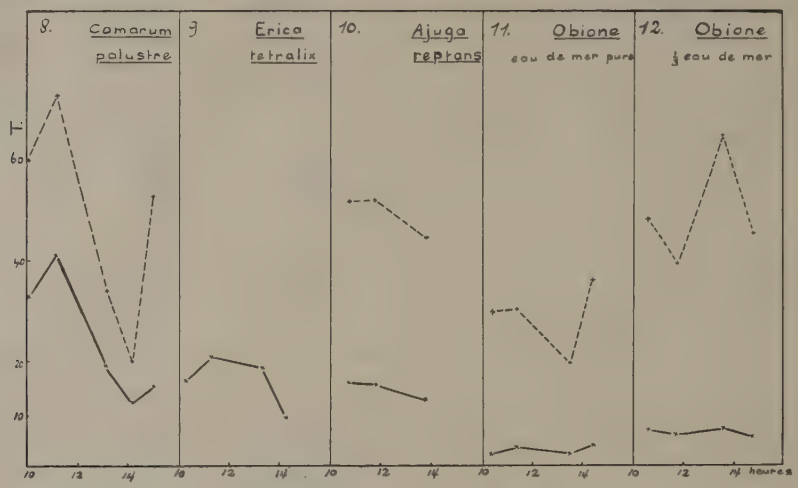

Fig. 8 à 12. Courbes journalières de la transpiration du 31 juillet 1934.

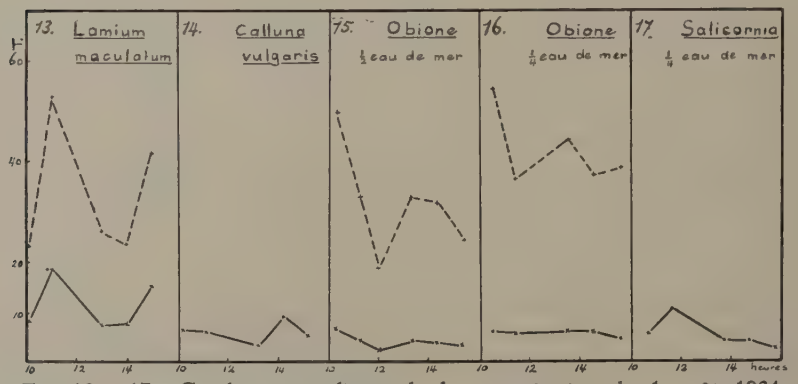

Fig. 13 à 17. Courbes journalières de la transpiration du 1 août 1934.

fonction de l'unité de surface est limitée aussi; pour les plantes halophiles cultivées dans le sol sablonneux dont la concentration des substances nutritives est égal à celle de l'eau de mer on trouve une valeur baucoup plus basse que chez les non-halophytes. Mes expériences donnent donc des résultats contraires à celles de STOCKER (12, 13).

5. *Conséquences en rapport avec la théorie de* SCHIMPER.

Dans la théorie de SCHIMPER les halophytes sont considérées comme des xérophytes qui limitent leur circulation d'eau non seulement parcequ'elles se trouvent sur un sol „physiologiquement sec" pour eux, mais aussi parceque leur structure serait xéromorphique. Cette dernière présomption est

inexacte : l'étude anatomique des halophytes ne met en évidence aucun des dispositifs susceptibles de limiter la transpiration comme on observe chez les xérophytes succulentes (CHERMEZON). Mais puisque la circulation d'eau est limitée chez les halophytes, ainsi que le démontrent mes mesures, et donnée la grande différence entre la transpiration des halophytes cultivées dans des concentrations différentes, il est possible que la constitution du sol rend difficile la résorption d'eau. En ce sens, le sol serait „physiologiquement sec".

SOMMAIRE.

1. La transpiration (mesurée par pesage de tiges coupées) chez *Obione portulacoides* et *Salicornia herbacea*, diminue à mesure qu'augmente la concentration des sels dans la rhizosphère (courbes 1 à 7).

2. Par comparaison avec quelques mésophytes les halophytes ont une transpiration limitée, que l'on exprime les résultats des mesures en fonction de poids frais, ou en fonction de l'unité de surface; mais dans ce dernier cas, les différences sont moins nettes (tableau, courbes 8 à 17).

Amsterdam, le 27 mai 1937. *Laboratoire de physiologie végétale de l'université.*

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Botany. — *Padang soil, an example of podsol in the Tropical Lowlands.* By H. J. HARDON. (From the Institute for Soil Science, Buitenzorg (Java).) (Communicated by Prof. L. G. M. BAAS BECKING.)

(Communicated at the meeting of May 29, 1937.)

In a recently published article I described some genuine podsol profiles from the Arfak Mountains of Northwestern New Guinea at about 2000 meters above sea level. Except for the absence of seasons the climate at this elevation is rather similar to a coastal or maritime one in the temperate zones. It is possible, however, as the evidence presented below shows, that true podsol, which occurs mainly in the climatic zone north of the 40th degree of latitude of the northern hemisphere, may develop, in distinct instances, in the tropical lowlands. There seems to be no doubt of this after studying some soil samples, collected by Dr. POSTHUMUS who accompanied Ir. H. WITKAMP, the geologist, during his visit to the Padang Loewai in the Koetai region of the residency S. E. Borneo.

Padangs (padang is the Malayan name for plain) are quartz sandy plains with an aberrant scanty flora, which has for many years interested botanists. VAN STEENIS has given a comprehensive compilation of the flora of the padangs in the different islands of the Malayan Archepelago. These padangs are known from Sumatra (KOORDERS, FREY—WYSSLING), Bangka and Billiton (VERBEEK, VALETON), Djemadja (VAN STEENIS), Western Borneo (COOMANS DE RUITER, POLAK), Middle Borneo (ENDERT), Southern Borneo (DIELS and HACKENBERG) and Celebes (MOHR). And RICHARDS has described similar plains in Sarawak.

VERBEEK supposed that the scanty and peculiar flora of the padangs in Bangka was due to the impermeability of the sandy hardpan, which he found below white sandy superficial layer and which was the result of cementation by organic acids. This layer corresponds to the horizon of consolidated brown sand which DIELS and HACKENBERG found at a depth of 150 cm in the sandy plains of South Borneo, and which is similar to the illuvial horizon of the usual temperate podsol profile. Dr. PENDLETON reports (personal communication) that in southern Siam along the coast of the Gulf, there are a number of similar padangs, which from field study seem obviously to be a tropical podsol.

It seems also that padangs are rather widely distributed in the Netherlands Indies and it is probable that on these poor quartz sandy plains podsolization is the general soil forming proces. I place below on record besides the results of the analyses of the soil samples from Padang Loewai, also those of samples from a padang in Bangka. I am much indebted to

Ir. A. BREGMAN, who was so kind as to very accurately sample some padang soil profiles and thus enabled me to extend these investigations.

Samples from a padang soil profile in Billiton, present in the collections of the Bodemkundig Instituut at Buitenzorg and from which the bleached layer has been formerly identified as „schierzand" (= Bleisand) were too small for a detailed analysis.

GEOGRAPHY. According to a description by Ir. H. WITKAMP the Loewai Padang is situated in the Koetai region of the residency of S. E. Borneo, near the equator at longitude 116° E., between the subdivision headquarters Melak, on the Mahakam, and Damai on the Kedang Pahoe, on the watershed between the two rivers.

The Loewai Padang is a somewhat undulating plain about 90 m above sea level, being a deposit of the Mahakam and possibly also partly of the Pahoe river. With an average width of 3 km this plain extends in a S. W. — N. E. direction for an unknown distance. On the slopes are some brownish coloured streamlets which flow out from the light coloured sandy soil and drain the higher land.

The padang in Bangka, from which samples have been studied, is situated near Aer Lajang, between Soengeiliat and Bakem. It is a flat, gently sloping, plain about 10 m above sea level. After heavy rains it is partly inundated, but during periods of drought the loose white sandy soil is very dry. VERBEEK, who visited these padangs about 40 years ago, supposed that they constitute what was formerly the shallow end of the Klabat Bay.

CLIMATE. On account of the low elevation the temperature is high, with only slight variations; the annual average is about 26° C. In the neighbourhood of the Loewai Padang rainfall observations have been recorded at Melak and Demai. As will be noted from table 1 the largest amount of rainfalls during the months of November, December, January and April with more than 300 mm each; the driest months being July, August and September with still an average of about 130 mm. The annual average is approximately 3000 mm.

For the northern part of Bangka, rainfall data are available for Belinjoe, north-west of the padang, and for Batoeroesa situated to the southeast. The months of greatest rainfall are December and January with more than 300 mm. each, while the driest months are June, July, August and September, although even during the dry season the monthly rainfall is more than 100 mm. As MOHR states, this means that throughout the year the rainfall exceeds the evaporation, so that the soil is constantly being leached.

VEGETATION. As POSTHUMUS studied in detail the peculiar flora of the Bornean Loewai Padang, we may briefly summarize his descriptions as follows:

TABLE I. Average monthly and annual rainfall in millimeters.

	Jan.	Febr.	Mar.	Apr.	May	June	Jul.	Aug.	Sept.	Oct.	Nov.	Dec.	Annual
Melak	332	271	259	370	332	246	116	144	152	227	354	353	3156
Damai	325	237	300	369	227	207	131	112	131	223	320	328	2909
Belinjoe	403	190	222	270	248	184	173	157	184	234	357	487	3109
Batoeroesa	333	228	269	239	205	160	139	127	110	157	222	310	2499

"The vegetation has much in common with that of other padangs. The country reminds one strongly of the European Heaths. It is an open plain with here and there groups of shrubs *(Tristana obovata, Vaccicium bancanum)* alternating with open spots of glittering quartz sand. There are also numerous orchids and ferns, the ant-plants *Hydnophytum, Myrmecodia* and *Dischidia* and the carnivorous *Nepenthes Reinwardtiana.* In the open spots are numerous lichens and sods of *Xyris complanata.*

VALETON has described the vegetation of the flora of the padangs on Bangka and VAN STEENIS quotes from that description as follows: "The white layer varies in thickness from ½—5 centimetres, and sometimes it is grey immediately below the surface, where fine black humus or mosses occur. The vegetation nowhere forms a compact mass or sod. Groups of low and high shrubs, generally with higher shrubs or small trees in the middle, alternate with a lower vegetation, which is always limited to separate spots or clumps, so that the white sand shows everywhere and in many places even predominates. Among the plants which were collected here the following are mentioned as characteristic: *Drosera Burmanni* in the dampest parts, forming dark areas when seen from a distance, often growing on the top of small colums of sand; *Fimbristylis* sp., *Rhynchospora* sp., *Xyris microcephala* and *X. bancana*".

He also mentions that on the lower-lying padangs *Baeckia frutescens,* which reminds one much of the Calluna of the European heaths, and which is also abundant in the podsol region of the Arfak mountains, forms more than half of the vegetation.

DESCRIPTION OF THE SOIL PROFILE. From Padang Loewai the samples of two profiles and from the padangs of Bangka those of six profiles have been studied (see table 1[A]). The profiles from each island were so similar in composition that for the sake of brevity only the analytical figures from the most representative profiles of each island need be recorded here.

LABORATORY INVESTIGATIONS. *Granular analysis.* Except for the samples of the superficial layers, which consist almost entirely of organic material and have not been analyzed, the results of the granular analysis of the samples of the two profiles are presented in table 2.

TABLE 1A.

	Sample number	Horizon	Depth	Description
Padang Loewai	41292	A_0	0—20 cm	Brownish black cover of half decomposed organic material.
	41293	A_2	10—120 „	Loose white quartz sandy layer.
	41294	B	120—170 „	Yellowish brown quartz sandy layer.
Padang on Bangka	57986	A_0	0— 10 cm	Black cover of half decomposed organic material intermixed with coarse quartz sand.
	57987	A_1	10— 25 „	Loose greyish black humic quartz sandy layer.
	57988	A_2	25— 40 „	Loose greyish white quartz sandy layer.
	57989	B_1	40— 70 „	Dark brown very compact quartz sandy hardpan.
	57990	B_2	70—100 „	Loose light brown quartz sandy layer.

TABLE 2. Granular composition (in percentages).

		Padang Loewai		Bangka padang			
size class \ horizon		A_2	B	A_1	A_2	B_1	B_2
2 mm	gravel	0	0	0	0.1	0.1	0.1
2—1 „	sand	1.2	1.2	0.2	0.4	0.4	0.3
1—0.5 „	sand	39.0	35.4	5.5	4.6	4.8	6.3
0.5—0.2 „	sand	47.0	49.0	52.3	36.6	42.8	51.7
0.2—0.1 „	sand	4.0	2.6	14.0	25.0	15.3	17.9
0.1—0.05 „	sand	6.1	5.7	23.6	27.4	23.6	15.9
0.5—0.02 „	silt	1.4	1.9	2.8	4.4	4.6	2.0
0.02—0.005 „	silt	0.9	1.6	0.6	1.0	1.3	0.5
0.005—0.002 „	clay	0.3	0.7	0.4	0.3	0.7	0.6
0.002—0.0005 „	clay	0.1	0.7	0.2	0.1	0.5	1.3
0.0005 „	clay	0.1	1.4	1.0	0.2	6.0	2.7

The Padang Loewai soil seems to be somewhat coarser than the Bangka soils.

The bleached layers show the highest percentages of sand while they have scarcely one percent of clay. The brownish coloured B-horizon contains more clay than the overlying bleached one, due to the presence of

the precipitated iron- and aluminium oxides and organic matter. Its percentage, however, is still very small, not exceeding ten percent.

The granular analysis gives sufficient information about the physical properties. Except the consolidated brown layer of the Bangka padang, which is undoubtedly the reason that damp places occur in the lower parts of this plain, this light textured soil must be pervious for rainwater.

Organic matter. A layer of halfdecomposed organic material, which covers the bleached white quartz sand occurs, especially under the bushes. In table 3 are summarized the results of the chemical analysis, made according to the methods of the Peat Experiment Station at Bremen, of the sample from the Padang Loewai.

TABLE 3. Chemical composition of the raw humus layer.

Sample number	loss on ignition	Ash	C	N	CaO	MgO	K_2O	P_2O_5	SiO_2
	Percentages of dry matter								perc. of ash
41292	66.57	33.43	33.71	0.59	0.00	0.02	0.05	0.03	89.63

The base content is exceedingly low; it is of interest to note that calcium, which averages 0,35 % in oligotrophic peat, was in this sample so small in amount it could not be determined. Magnesium and potassium occur only in very small quantities. The C/N ratio of 57 is very high. Since Dr. POSTHUMUS could not locate any traces of forest burning, this high ratio cannot be caused by charcoal. Moreover this soil is so poor in plant nutrients that the natives never think of cultivating it. Therefore the high C/N ratio must be ascribed to the incomplete humification and also to the presence of undecomposed organic materials.

In contrast to the horizon of accumulation where the aluminium- and iron-humates are precipitated, and which contains 1.2 % of organic matter, the bleached zone underlying the raw humus cover only shows 0.1 % of organic matter. The hardpan of the Bangka profile contains much more organic matter, amounting to 5.2 %. This matter cements the sand particles of this layer. The nitrogen content of this organic matter is very low, finding its expression in the high C/N ratio of 77.

The reaction of the profile. The acidity of the raw humus covers of the two profiles is high, the pH being lower than 3. The pH of the bleached layer is rather high, probably due to the almost total absence of colloidal material. The B-horizon, which contains much more clay, shows a lower pH, especially the hardpan of the Bangka profile, which in addition to more clay contains high percentage of humic acids.

As would be expected from the small clay fraction the hydrolytic acidity

of the A_2-layer is low, increasing in the underlying B-horizon, which must be ascribed, at least in part, to the organic complex component of this layer. Only the samples of the B-horizon gave any exchange acidity at all; the bleached layers did not give enough to measure.

TABLE 4. pH, hydrolytic and exchange acidity.

Horizon	pH		Hydrolytic acidity		Exchange acidity	
	Padang Loewai	Bangka	Padang Loewai	Bangka	Padang Loewai	Bangka
A_0	2.8	2.7	—	—	—	—
A_1	—	3.9	—	15.7	—	0
A_2	6.1	6.1	2.3	4.0	0	0
B_1	5.4	3.9	22.7	122.4	1.0	16.8
B_2	—	4.6	—	42.7	—	3.1

Chemical features of the soil. To ascertain the "total" phosphoric acid and base content of the soil the samples were extracted at room temperature with 25 % hydrochloric acid. Following TAMM's method an acid solution of ammonium oxalate was used in the determination of the mixed inorganic colloids of aluminium and iron oxide and silica. The results of these analyses are given in table 5.

TABLE 5. Chemical composition of the soil (in percentages).

Horizon	P_2O_5		Cao		MgO		K_2O		SiO_2		Al_2O_3		Fe_2O_3	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
A_1	—	0.002	—	0.022	—	0.009	—	0.001	—	0.06	—	0.32	—	0.05
A_2	0.001	0.001	0.008	0.032	0.009	0.007	0.024	0.002	tr.	0.08	0.06	0.27	0.03	0.03
B_1	0.004	0.005	0.002	0.029	0.002	0.002	0.025	0.004	0.03	0.14	0.64	1.58	0.91	0.07
B_2	—	0.007	—	0.035	—	0.007	—	0.004	—	0.22	—	1.66	—	0.24

I = Padang Loewai; II = Bangka.

The content of phosphoric acid is low, especially in the bleached layer. The percentages of calcium and magnesium, which are exceedingly low as compared with other tropical soils, in the bleached horizon are somewhat higher than in the underlying brown horizon. The potassium content of the samples from Padang Loewai is rather high, possibly due to the presence of small quantities of potassium bearing feldspar.

As may be expected, the ammonium oxalate extracts of the samples of the bleached horizons are very low in sesqui-oxides, the content being much higher in the zone of accumulation. The brown colour of the B_1-

layer of the Padang Loewai profile is chiefly caused by iron oxides, while the samples of the hardpan of the Bangka soil yielded only minute quantities of these oxides. In the zone underlying the hardpan, however, the iron oxide-content is much higher. The rather low percentage of iron oxide in the hardpan is probably due to reduction processes which take place in the presence of the large quantities of humic acids, during the temporarily submerged conditions after heavy rainfall. Moreover the acidity of this layer is so high that iron humates, leached from the eluvial zone, do not precipitate and will be partly carried away by the water in the small streams which have their source in the lower parts of the padang, or will be precipitated in the underlying, less acid, B_2-horizon. The content of aluminium oxide of the B-horizon is high as compared with that of the bleached layer.

The leaching of the sesquioxides from the A-horizon and the precipitation of these oxides in the B-layer may be clearly illustrated by the results of the chemical composition of the colloidal fractions ($< 2\,\mu$) of the samples of the Bangka podsol, as shown in table 6.

TABLE 6. Silica and base content of the clay fraction ($< 2\,\mu$) (in percentages)

Horizon	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	$\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ (mol. ratio.)
A_0	48.94	18.84	6.37	10.07	0	5.25	3.42	0.46	5.45	3.62
A_1	60.63	12.34	3.14	14.16	0	4.69	2.50	0.09	1.82	7.17
A_2	65.20	10.12	4.20	8.62	0	4.58	4.35	0.27	2.12	8.64
B_1	18.22	70.75	4.42	2.69	0	2.00	0.05	0.18	1.05	0.42
B_2	14.01	73.21	6.50	2.71	0	0.99	0.10	0.23	1.24	0.31

The SiO_2-sesquioxides ratio, already high in the colloidal fraction of the superficial layer, increases in the underlying A-horizons, due partly to the loss of iron and aluminium, partly to the contamination with finely divided free SiO_2. As is to be expected the B-layers show a low ratio.

Discussion. The process of podsolization is intimately related to the presence of an acid humus cover. The humic acids, originating from the organic material of this layer, dissolve the sesquioxides from the superficial soil so that they may be carried downward by percolating water to the depth, where they are precipitated. Generally, however, the mineralization of the organic material at the temperature of the tropical lowlands proceeds so rapidly, that acid humus is rather seldom formed under aerobic conditions.

In regions with heavy rainfall throughout the year, on pervious sandy quartz soils, which do not allow capillary rise of the groundwater and

which are poor in bases, it is evident that the formation of this kind of humus may take place. The bases set free by the mineralization of the organic material will be soon removed, leaving humic matter which is poor in bases. Moreover the base content of the vegetation on these poor soils is much less than that on richer soils, as is shown by the results of the analyses in table 7 of leaves [1]), both of the same plant species, from the padangs and from the Botanic Garden at Buitenzorg (andisitic lateritic soil).

TABLE 7. Chemical composition of the leaves of Dacrydium elatum and Rhodomyrtus tomentosa from padangs and from the Botanic Garden at Buitenzorg. (Percentages of dry matter).

	Dacrydium elatum		Rhodomyrtus tomentosa	
	Padang	Botanic Garden	Padang	Botanic Garden
ash	2.16	7.59	2.58	3.70
CaO	0.59	3.43	0.13	0.58
MgO	0.33	0.69	0.21	0.35
K_2O	0.52	0.57	0.36	0 50
Na_2O	0.08	0 05	0.24	0.14
MnO	0.02	0.15	0.07	0.45
P_2O_5	0.10	0.15	0.07	0.45

The four factors mentioned, viz. a pervious soil, a soil poor in bases, a constant heavy rainfall and a small base content of the vegetation, make possible the formation of acid humus in the tropical lowlands. The high acidity of the humus in turn causes a partial sterilization and also delays the speed of mineralization, resulting in an accumulation of raw humus under aerobic conditions even in this tropical climate.

The presence of the acid raw humus cover is the cause of the podsol process which, as described in this paper, takes place in the padang soils.

It is remarkable, however, that the most typical zonal soil type may occur extensively as an intrazonal soil, in regions where the climatic factors would not normally favour its formation. Many factors, climatic, geologic, topographic, and biotic, must coordinate to cause the development of this soil type.

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[1]) The leaf-samples are from the Herbarium of the Botanic Garden at Buitenzorg, selected by the botanist Dr. C. G. G. J. VAN STEENIS.

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Histology. — *Der Rhythmus des Glykogengehaltes der Leber der weissen Maus, dargestellt durch die Stufenzählmethode.* Von GOTTWALT CHRISTIAN HIRSCH und R. F. J. VAN PELT. (Aus dem Labor. für exper. Histologie des Zoolog. Institutes d. Univ. Utrecht; Leiter: G. C. HIRSCH). (Communicated by Prof. H. F. NIERSTRASZ).

(Communicated at the meeting of May 29, 1937.)

Die Leber der Säugetiere besitzt allem Anschein nach einen Arbeitsrhythmus. So fand E. FORSGREN 1927 beim *Kaninchen* einen merkwürdigen Antagonismus zwischen dem Aufbau und Abbau des Glykogens einerseits und dem Aufbau der Gallengranula andererseits: wenn die Leber das Stadium einer maximalen Glykogenbereitung durchläuft, dann ist gerade die Bereitung von Gallengranula auf dem Minimum angelangt und umgekehrt. Hunger- und Fütterungszeiten sollen keinen Einfluss auf diese rhythmische Aktivität der Leber haben. FORSGREN meint vielmehr, dass hier ein Eigenrhythmus der Leber zu Tage trete: bei den Kaninchen wenigstens soll das Maximum an Glykogen um etwa 9—10 Uhr gefunden werden, das Minimum bei 14—16 Uhr. Doch scheinen hier noch erhebliche

Schwankungen vorzuliegen, denn in einer Untersuchung, die FORSGREN im folgenden Jahre publizierte, gibt er zwei tägliche Maxima um 2 oder um 14 Uhr an.

Im Jahre 1931 erschien eine ähnliche Untersuchung von A. HOLMQUIST, welche *an Ratten* angestellt wurde. Auch hier wurden 2 Glykogenmaxima gefunden etwa um 21 und 4 Uhr; doch schien das eine Maximum dem Verf. selbst etwas zweifelhaft.

Und schliesslich hat NOEL 1923 an der Leber von *weissen Mäusen* die ersten Beobachtungen eines schwankenden Gehaltes an Mitochondrien und Glykogen gemacht, ohne noch zu genaueren Resultaten zu kommen. Erst ÅGREN, WIELANDER und JORPES haben 1931 *chemisch* nachgewiesen, dass die Glykogenmenge in der Leber einem täglichen Rhythmus unterworfen ist: Der Rhythmus zeigt nur *ein* Maximum und *ein* Minimum binnen 24 Stunden: das Minimum des Glykogengehaltes liegt zwischen 10 und 18 Uhr; das Maximum liegt zwischen 23 und 6 Uhr [1]); d.h. grob ausgedrückt: in der Nacht wird Glykogen aufgebaut, am Tage wieder abgeschieden.

Dies würde schön zu den physiologischen Vorstellungen passen, dass durch die erhöhte Aktivität der Tagesphase Glykogen ausgeschüttet wird, in der Nacht dagegen aufgebaut. Doch kann man über die Faktoren zunächst noch nichts aussagen. Hunger und Fütterung spielen hier wahrscheinlich keine Rolle; dagegen zeigten die Mäuse eine erhöhte Resistenz gegenüber Insulin am Nachmittag und teilweise auch während der Nacht (ÅGREN, WILANDER und JORPES).

Diese Untersuchung wurde 1931 von HOLMGREN histologisch ergänzt. Er schätzte in seinen mikroskopischen Praeparaten die Menge des Glykogens (und der Gallengranula) und kam zu dem Ergebnis, dass ÅGREN, WIELANDER und JORPES wahrscheinlich Recht hatten.

Dies sind sehr interessante Rhytmen, denen wir im Laufe der nächsten Jahre näher nachgehen werden. Doch bevor wir in eine Faktorenanalyse des Leberrhythmus eintreten, war es unsere Aufgabe, die nötigen exakten Grundlagen für eine Messung des Rhythmus zu schaffen. Denn ein Rhythmus ist das gesetzmössige Schwanken einer *Masse*: wollen wir demnach einen Rhythmus irgend eines Organes beweisen und dann analysieren, so müssen wir eine *Masse* untersuchen; dies aber können wir nur durch wägen oder zählen. Das wird wohl mal vergessen.

Die bisherigen Untersuchungen des Rhythmus des Leberglykogens basieren alle auf der chemischen quantitativen Extraktion. HOLMGREN untersuchte zwar 1931 *histologisch*, hat aber keine quantitativen Methoden dabei angewendet, sondern basiert auf ÅGREN usw. Uns scheint aber gerade die Anwendung histologisch-quantitativer Methoden zur Erken-

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[1]) Es ist leider H. HOLMGREN (1931) bei der Wiedergabe der Kurven von ÅGREN, WIELANDER und JORPES ein störender Fehler unterlaufen, indem er die Tageszeiten „am" und „pm" verwechselt hat. Darauf dürfen wir wohl eben aufmerksam machen.

nung eines Organrhythmus notwendig, weil auf diese Weise Zusammenhänge entdeckt werden können, die der nur-chemischen Analyse verborgen sind.

Wir wollten deswegen versuchen, ob es nicht möglich wäre, durch die 1913 bis 1929 von G. C. HIRSCH ausgearbeitete histologische Stufenzählmethode zu exakten Ergebnissen zu kommen. Denn die Schätzungen von HOLMGREN erschienen uns als Methode noch keine Basis für weitere Experimente zu sein, weil sie zu verschwommen ist. HOLMGREN gebraucht zur Schätzung z.B. die Ausdrücke: „Glykogen in reichlicher Menge", oder „in mässiger Menge" oder „augenscheinlich weniger Glykogen", „augenscheinliche Vermehrung". So wertvoll solche Schätzungen sein können zur Bildung von Hypothesen, als eine Basis zu einer genaueren Bestimmung des Rhythmus und zur Lösung der Frage der Faktoren dieses Rhythmus kann diese Schätzungsmethode doch nicht dienen.

Bevor wir aber zur eigentlichen Analyse schreiten, musste also erst die Frage untersucht werden, ob man durch die histologische Stufenzählmethode zu einer ebenso genauen Messung des Glykogens kommen kann wie durch die chemische Methode.

Technik.

Wir arbeiteten nur an weissen Mäusen, die vollkommen gesund waren. Wir gebrauchten erstens eine Gruppe von 39 weissen Mäusen welche demselben Stamme entsprangen und welche am 10. und 31. März fixiert wurden [1]); zweitens eine Gruppe von 16 Mäusen aus zwei Stämmen, welche am 14. Februar fixiert wurden. Die Geschlechter waren ungefähr zu gleichen Teilen vertreten. Kleine Leberstücke wurden in Carnoy fixiert. Um zu sehen, welchen Einfluss die Dicke des fixierten Objektes und damit die Schwierigkeit des Eindringens des Fixators auf die Berechnung des Glykogens haben könnte, haben wir die erste Gruppe von 39 Mäusen in zwei Untergruppen geteilt: von der einen Gruppe wurde 2 mm dicke Leberscheiben fixiert, bei der anderen dagegen 5 mm dicke Scheiben. Nach der Fixation wurde in Celloidin eingebettet, daraufhin in Paraffin. Die Schnittdicke muss wenigstens 10 μ betragen, sonst kann eine Zählung nicht gleichmässig durchgeführt werden. Gefärbt wurde mit BEST's Karmin.

Die Tiere wurden gefüttert in regelmässigen Zeiten mit einer gleichmässigen Menge von Brot, das in gekochter Milch getränkt wurde.

Methodik.

Es wurde probiert, eine Zählmethode zur quantitativen Bestimmung des Glykogens anzuwenden. Zu dem Zwecke wurde 4 Stadia der Glykogenaufstapelung in den Zellen unterschieden:

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[1]) Wir sind Herrn Prof. DE BLIECK und Prof. NIESCHULZ sehr dankbar für die Ueberlassung dieser für unsere Zwecke ausgezeichneten Mäuse.

Stadium *a* (Abb. 1): Zellen, die ganz oder beinahe ganz mit Glykogen gefüllt waren.

Stadium *b* (Abb. 2): Zellen, die zum grössten Teile mit Glykogen gefüllt sind.

Stadium *c* (Abb. 3): Etwa die Hälfte bis ein Viertel der Zellen ist mit Glykogen gefüllt.

Stadium *d*: Die Zellen sind leer.

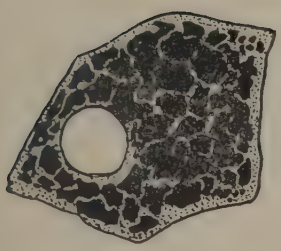

Abb. 1. Stadium *a* der Leberzelle der weissen Maus: Die Zelle ist beinah ganz mit Glykogen (schwarz) gefüllt.

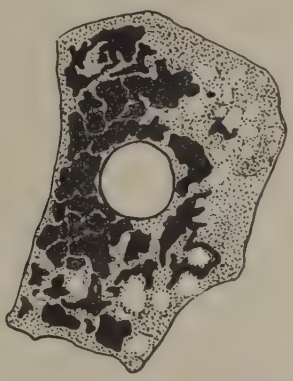

Abb. 2. Stadium *b*, eine Zelle, die zum grössten Teile mit Glykogen gefüllt ist.

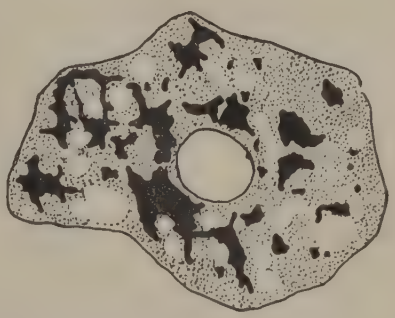

Abb. 3. Stadium *c*: die Hälfte bis ein Viertel der Zellen ist mit Glykogen gefüllt.

Die Berechnung geschah möglichst objektiv:, wir fügten in das Okular eine Nadel ein und bewegten das Objekt mit einem beweglichen Mikroskoptisch. Nur diejenigen Zellen, deren Kerne durch die Nadel bei der Bewegung getroffen waren, wurden gezählt. Zuerst wurden die Prozente der vier angegebenen Stadien gezählt und dann prozentualiter berechnet (Abb. 4 und 5). Schliesslich versuchten wir, den Gehalt der ganzen Leber auf Grund dieser prozentualen Berechnungen kurvemässig wieder zu geben (Abb. 6). Zu diesem Zwecke haben wir die errechneten Ziffern für das Stadium *a* mit 3 multipliziert, von *b* mit 2, von *c* mit 1 und die Anzahl der Zellen des Stadiums $d = 0$ gestellt.

Ergebnisse der Zählungen.

Die Kurven der *Stadien a* (voll mit Glykogen) und Stadium *c* (etwa die Hälfte der Zelle ist gefüllt mit Glykogen) ergaben keine deutlichen Kurven, weil das Stadium *a* zu selten vorkommt, um wichtige Ausschläge zu zeigen, und weil das Stadium *c* zu viel vorkommt, um einen Rhythmus deutlich zu machen. Das *Stadium c* kommt nämlich beinahe gleichmässig vor, auf- und niederschwankend zwischen etwa 20—60 % der Zellen. Es ist charakteristisch für solche quantitativen Berechnungen histologischer Art, dass die mittleren Stadien oft kein deutliches Bild des Arbeits-

rhythmus geben, weil sie gleichmässig schwanken. Das liegt wahrscheinlich daran, dass jede Zelle bei dem Glykogenabbau und bei der Bereitung das Gleichgewicht einer mittleren Glykogenmenge in Kürze erreicht. Wir haben infolgedessen die Stadien *a* und *c* nur bei dem Totalergebnis in

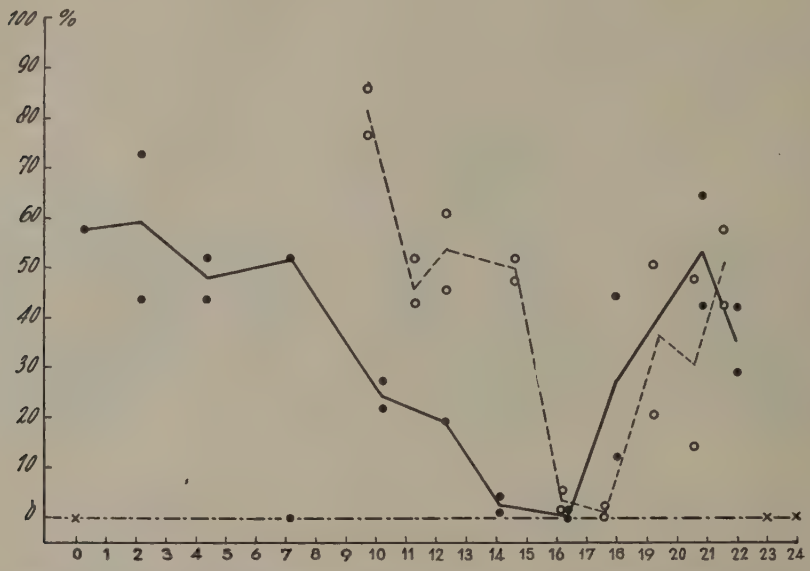

Abb. 4. Ordinate: die Prozentsätze der Zellen im Stadium *b*: also mit viel Glykogen beladen. Abscisse: die 24 Stunden des Tages. Schwarzer Kreis: die Leberstücke wurden 5 mm dick fixiert; heller Kreis: die Stücke wurden 2 mm dick fixiert.

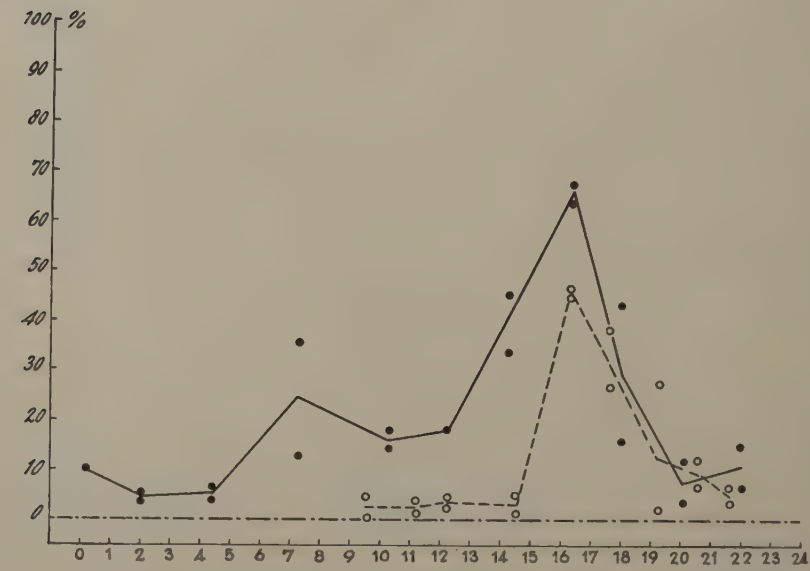

Abb. 5. Prozentsätze der Zellen des Stadiums *d*: die Zellen enthalten kein Glykogen. Zur weiteren Erklärung vergleiche Abb. 4.

Betracht gezogen und beistehend nur die Stadien *b* und *d* graphisch wiedergegeben, welche beide extreme Zustände der Zellen sind.

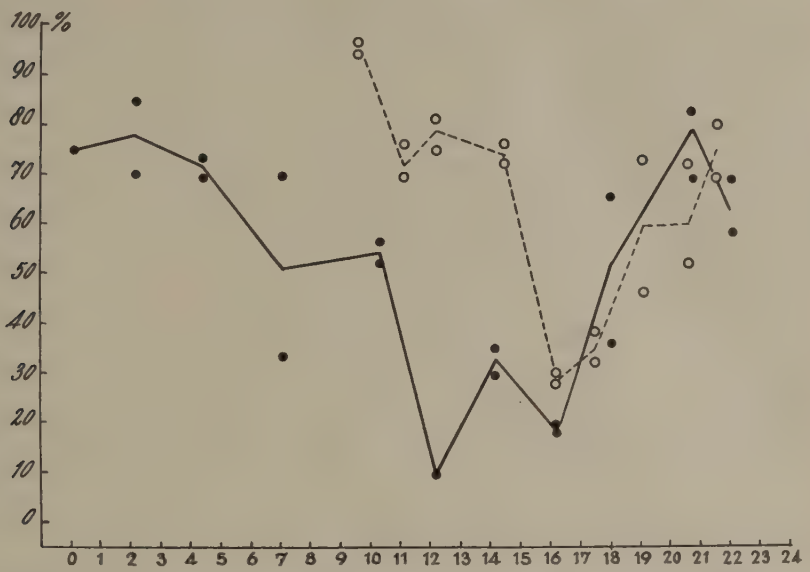

Abb. 6. Der Totalgehalt einer Mäuseleber an Glykogen. Die Berechnung der Punkte siehe im Text. Weitere Erklärungen der Zichen vergleiche in Abb. 4.

Die Ergebnisse können zunächst folgendermassen beschrieben werden:

1. Das Stadium *b* (Abb. 4), welches wahrscheinlich auf Grund einer starken Insulinausschüttung *viel* Glykogen enthält, zeigt ein deutliches *Maximum in den Nachtstunden 20—2 Uhr und ein Minimum bei 12—17 Uhr*. Die Ausschläge der Kurven sind viel grösser als bei der chemischen Analyse von ÅGREN.

2. Das Stadium *d* (Abb. 5), in welchem *kein* Glykogen in den Zellen anwesend ist, zeigt den dazu passenden reziproken Wert.

3. Die Berechnung des totalen Glykogens (Abb. 6) ergibt dieselben Ergebnisse auch nach Hinzufügung der errechneten Werte von *a* und *c*. Auch hier sind die Ausschläge der Kurve sehr gross.

Damit ist die chemische Untersuchung von ÅGREN, WIELANDER und JORPES 1931 bestätigt; diese fanden das Maximum an Glykogen zwischen 23 und 6 Uhr, wir dagegen zwischen 20 und 2 Uhr; das Minimum fanden die schwedischen Untersucher zwischen 10 und 18 Uhr, wir dagegen zwischen 12 und 17 Uhr. Wir unterscheiden uns also nur etwas in der Breite des Zeitraumes, in welchen das Maximum oder Minimum fällt; dieser Unterschied ist vorläufig noch nicht wichtig.

4. Noch etwas Anderes ergibt sich aber hinsichtlich der Frage: ist diese Stufen-zählmethode geeignet, um eine ebenso genaue Basis zu bilden, wie die chemische Methode. Die Streuung der Ergebnisse der chemischen Bestimmung ist gross. Bei unseren Ergebnissen ist sie auch ansehnlich, aber kleiner. Es tritt also innerhalb einer sonst homogenen Mäusegruppe

eine individuelle Streuung auf, welche auch die Breite der Minima und Maxima beeinflusst. Die Streuung ist aber bei der chemischen Methode und bei der histologischen Stufen-Zählung zurück zu führen auf individuelle Unterschiede. Also sind beide Methoden gleichwertig; wir können also die histologische Stufenzählmethode für die Glykogenbestimmung der Leber mit demselben Rechte anwenden, wie die chemische Extraktionsmethode. Wir haben aber bei der *histologischen Stufenzählmethode den Vorteil,* eine geringere Streuung und höhere Ausschläge zu haben und auch im histologischen Bilde die cytologische Struktur *neben* den Zählungen beobachten zu können, während die chemische Methode uns nur ein einziges Faktum berichtet.

Der Einfluss der Schnittdicke auf die Ergebnisse der Stufenzählmethode.

Hinsichtlich der histologischen Stufenzählmethode bedarf es aber noch einiger Hinweise auf bestimmte *Kautelen,* die man hierbei im Auge behalten muss. Wir haben, wie wir oben schon sagten, die 39 Tiere in zwei Gruppen geteilt, und in dem einen Falle Leberstückchen von 5 mm Dicke fixiert, bei der anderen Gruppe dagegen von 2 mm Dicke. Wir haben diese Gruppen in unseren Kurven ebenfalls unterschieden, indem die Ergebnisse an Praeparaten aus dicken Schnitten mit einem schwarzen Punkt, die aus dünnen Schnitten mit einem kleinen Kreis angedeutet wurden. Die mittleren Werte dieser beiden verschiedenen Gruppen sind bei 5 mm Stückdicke durch einen Strich, bei 2 mm Stückdicke durch eine Strichlinie angedeutet. Es ist auffallend, dass sich zwischen beiden Kurven ein Unterschied ergibt: die Ergebnisse aus Stücken, welche 5 mm dick waren, sind im grössten Teil der Fälle niedriger als die Ergebnisse aus dünneren Stücken; nur an der rechten Seite der Kurven verändert sich das Bild etwas und die Ergebnisse laufen ungefähr parallel.

Wir möchten auf diesen Unterschied besonders hinweisen. Er kann folgendermassen erklärt werden: die fixierte Flüssigkeit dringt nur langsam ein, sodass die in der Mitte liegenden Zellschichten der 5 mm dicken Schnitte Zeit haben, das vorhandene Glykogen aufzulösen, sodass es nicht mehr so reichlich vorhanden ist, wenn das Fixiermittel die mittleren Zellschichten erreicht. Das ergab sich auch aus den histologischen Gesamtbildern, welche wir erhielten. Wir müssen also bei der Anwendung der Stufenzählmethode auf drei Dinge achten: einmal auf die gleichmässige Dicke der Fixierstücke, 2. darauf, dass die Fixierstücke nicht dicker sind als 2 mm und schliesslich auf die Dicke der Paraffinschnitte, die nicht dünner sein sollen als 10 μ.

Steht der Rhythmus des Glykogens bei den weissen Mäusen fest?

Von 39 Tieren, welche gleichen Ursprungs waren und alle am *10. und 31. März* untersucht wurden, haben wir die vorstehenden Kurven entworfen. Ist die Streuung der Ergebnisse auch ansehnlich, d.h. besteht

auch eine individuelle Schwankung, so sind die Ausschläge der Kurven doch andererseits so gross, dass ein deutlicher Leberrhythmus bei den weissen Mäusen sich zeigt. Wir dürfen aber nicht verschweigen, dass wir 16 Mäuse angetroffen haben, welche von zwei verschiedenen Stämmen herstammten: 7 Mäuse kamen aus demselben Stamme wie die verwendeten 39 Mäuse, 9 Mäuse kamen aus einem anderen Stamme. All diese Tiere waren durcheinander am *13. und 14. Februar* getötet. Diese 16 „Februartiere" zeigen eine Verschiebung ihrer Maxima und Minima gegenüber den oben berechneten 39 „Märztieren". Wir haben noch nicht genügend Material, um hier schon eine gut fundierte Kurve zeigen zu können, aber wir können aus den 16 gewonnenen Punkten bereits vorsichtig schliessen, dass das Maximum des Glykogens etwa in der Zeit von 3—8 Uhr morgens liegt, also zu einer Zeit, in welcher das Maximum der Gruppe von 39 „Märztieren" bereits im Absinken begriffen ist. Das Minimum an Glykogen liegt sehr wahrscheinlich ebenfalls verschoben am Abend bis in die Nacht hinein. Es hat also bei dieser zweiten Gruppe von 16 „Februarmäusen" sehr wahrscheinlich eine *Verschiebung des Maximums um einige Stunden vorwärts* stattgefunden.

Wir können vorläufig noch nicht mit Sicherheit sagen, worauf diese Verschiebung beruht; diese Frage soll demnächst analysiert werden zusammen mit einer Aufhellung der Faktoren, welche den Arbeitsrhythmus der Leber hervorrufen.

Aber angesichts der Tatsachen: 1. dass die 16 „Februarmäuse" von zwei verschiedenen Stämmen entsprangen und doch den gleichen oder wenigstens einen sehr ähnlichen Rhythmus zeigen;

2. dass alle „Februarmäuse" unter gleichen Bedingungen gehalten wurden wie die „Märzmäuse" (Futter, Wohnort);

3. dass beide Gruppen sich unterscheiden durch einen jahreszeitlichen Unterschied von vier bis 6 Wochen auf der Grenze zwischen Winter und Frühling — all dies spricht für die *Hypothese*, dass die Verschiebung der Maxima: bei den „Februartieren" später, bei den „Märztieren" früher, *im Zusammenhang stehen dürfte mit der Jahreszeit*. Dann würde die Verfrühung der Maxima bei den „Märztieren" wieder mit der erhöhten Aktivität des Darmtraktus im Frühjahr zusammenhängen wie dies HIRSCH und JACOBS 1930 für den Darm von Astacus nachwiesen.

Zusammenfassung.

Es wurde die Frage geprüft, ob die histologische Stufenzählmethode bei der Berechnung des Gehaltes einer Leber an Glykogen ebenso zuverlässige Ergebnisse liefert, wie die chemische Untersuchung. Die Stufenzählmethode wurde dadurch angestellt, dass vier verschiedene Stadien des Glykogengehaltes in den Zellen (Abb. 1—3) ausgezählt wurden. Es ergab sich, dass die Streuung der Ergebnisse auf Grund der individuellen Schwankungen etwas geringer ist wie bei der chemischen Methode, doch sind die Ausschläge der Stufenzählmethoden-kurven grösser. Beide Me-

thoden können in gleicher Weise angewendet werden. Die Kurven zeigten weiterhin, dass die Dicke der fixierten Stücke dadurch von Einfluss auf die Zählung ist, dass die inneren Zellen des Stückes ungenügend fixiert sind; man darf die Stücke nicht dicker als 2 mm nehmen. Auch dürfen die Paraffinschnitte nicht dünner sein als 10 μ. Es wurden mit Hilfe dieser Stufenzählmethode die chemischen Ergebnisse von ÅGREN, WIELANDER und JORPES 1931 bestätigt, und zwar in diesem Sinne: das Maximum an Glykogen findet sich im März zwischen 20 und 2 Uhr, das Minimum zwischen 12 und 17 Uhr. Ein gewisser Unterschied in der Breite der Maxima und Minima spielt keine Rolle bei der Beurteilung.

Dieser Gruppe von „Märzmäusen" stand aber eine Gruppe von 16 „Februarmäusen" gegenüber, welche aus zwei verschiedenen Stämmen stammten und 4—6 Wochen vor den „Märzmäusen" getötet wurden. Diese zeigten eine Verschiebung des Maximums und Minimums um einige Stunden vorwärts: nämlich in die Zeit zwischen 2 und 8 Uhr und in die späte Abendzeit. Worauf diese Verschiebung zurückzuführen ist, muss noch weiter analysiert werden; aber man kann mehrere Gründe dafür angeben, dass es die Jahreszeit ist, welche die Verschiebung des Rhythmus verursacht: wahrscheinlich sind Wintertiere etwas später, Frühlingstiere etwas früher in den Maxima ihres Glykogenrhythmus.

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Physiology. — *Studies on phosphorus metabolism in normal and rachitic rats with a radioactive phosphorus isotope.* By M. J. L. DOLS and B. C. P. JANSEN. (Laboratory of Physiological Chemistry, University Amsterdam) and G. J. SIZOO and J. DE VRIES. (Natuurkundig Laboratorium, Vrije Universiteit, Amsterdam). (Communicated by Prof. G. GRIJNS).

(Communicated at the meeting of May 29, 1937.)

Introduction.

It is a matter of common knowledge, that vitamin D plays an important part in Ca- and P-metabolism. However, the characteristic mode of action of this vitamin is still obscure. A group of authors consider the vitamin D only as a factor influencing the Ca and P balance, either by increasing absorption, or by diminishing excretion. Others however think the vitamin acts on the deposition of Ca and P into the bone. But, it is also possible that it acts in all an other way. The study of this question was very difficult as it was impossible to establish, whether the minerals in the body come from the just administered food, or they were already present in the body. However, the recent progress in the production of artificial radioactive isotopes here opens up new ways. At present the radioactive isotope of phosphorus $^{32}_{15}P$ is easily accessible, whereas the half value period is long enough (15 days) to use this isotope in physiological work. With this isotope it is possible to "label" the phosphorus of the diet and to follow this "labelled" phosphorus on its way through the organism.

The use of radioactive isotopes as indicators in physiological-chemical determinations is not new at all, since BEHRENS [1]) used thorium B as an indicator in his investigations on the distribution of lead in the organism. CHIEVITZ and HEVESY [2]) were the first, who used a radioactive indicator in the study of phosphorus metabolism in rats. In a recent paper [3]) a detailed account of these investigations was given, which were carried out chiefly on rats but partly also on human beings. A general account on the use of isotopes as indicators in biological research was published recently by KROGH [4]).

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[1]) B. BEHRENS, Arch. f. Exper. Pathol., **109**, 332 (1925).
[2]) O. CHIEVITZ and G. HEVESY, Nature, **136**, 754 (1935).
[3]) O. CHIEVITZ and G. HEVESY, Kgl. Danske Vid. Selsk., Biol. Medd., **13**, 9 (1937).
[4]) A. KROGH, Science, **85**, 187 (1937).

We wish to publish here a full survey of our experiments [5, 6]) set up in 1936 with the object to study the influence of vitamin D on the absorption, retention and deposition in bone of normal, rachitic and "treated" animals. The "treated" animals were those rachitic rats, which received a large dose of vitamin D (30 Int. Units as halibutoil) a few hours before the oral administration of the "labelled" phosphorus. The rats used were of the albino type; they were rendered homozygote as far as possible by inbreeding. They were weaned on the 21st day and then used in the experiments. Most of them then had a weight of 35—40 grams. Every rat was kept in a zinc cage with a crossbarred floor; coprophagy thus being impossible. The rats were devided into three groups and placed in a room from which all daylight was excluded. All groups were fed for 28 days the STEENBOCK-BLACK diet. Besides the check group received 3 times a week a sufficient dose of halibut oil, whereas the other rats only got a solution of carotene in peanut oil. After 28 days the rats were x-rayed to check the diets and thereupon used in these experiments.

The preparation of the labelled phosphorus.

The radioactive phosphorus $^{32}_{15}P$ was obtained by neutron bombardment of sulphur according to the nuclear reaction

$$^{32}_{16}S + ^{1}_{0}n \rightarrow ^{32}_{15}P + ^{1}_{1}H.$$

The sulphur was thoroughly purified by means of continuous extraction with a mixture of carbondisulphide and carbontetrachloride (1 : 2) in a Soxhletapparatus. Then it was placed round the neutron source, consisting of 100 mg. Ra mixed with beryllium powder. This neutron bombardment lasted about twenty days. Then a minute quantity of red phosphorus was added to the sulphur (about $1 : 10^4$) to facilitate the separation of the active isotope. Thereupon this sulphur-phosphorus mixture was combusted in a stream of oxygen. The apparatus used is represented by fig. 1. The

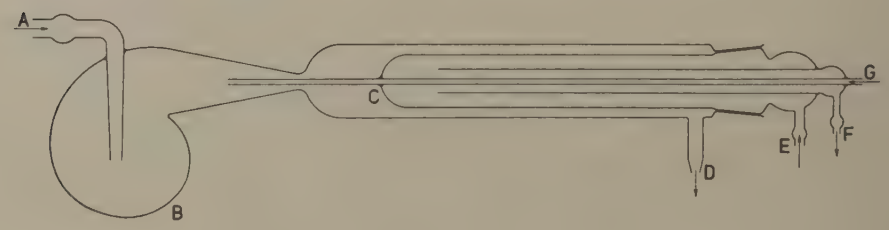

Fig. 1.

[5]) M. J. L. DOLS, VI. Weltgeflügelkongress, Berlin-Leipzig, Ber. **3**, 198 (1936).
[6]) M. J. L. DOLS, B. C. P. JANSEN, G. J. SIZOO and J. DE VRIES, Nature, **139**, 1068 (1937).

SO_2 escaped at D, whilst the P_2O_5 together with a little SO_3, was mainly condensed at the cooling tube C.

After the apparatus was washed out with distilled water a solution of phosphoric- and sulphuric acid was obtained. The solution was defiled with carbon rests, due to the carbon disulphide taken up by the sulphur. After these rests had been removed by filtration the solution could be worked up.

The most convenient way to separate the phosphorus would have been to precipitate it in a solid form, e.g. as $MgNH_4PO_4$. However, it is very difficult to insert a solid preparation into the stomach. Besides it is a wellknown fact that magnesium can influence the Ca- and P-metabolism. Therefore it was not desirable to use this salt. The most suitable form in which the phosphorus can be administered is a solution of sodium phosphate.

In preliminary experiments the phosphorus was precipitated from the solution as $MgNH_4PO_4$, boiled up with sodium carbonate and filtrated. About 60 % of the labelled phosphorus was found back in the filtrate. To get a sufficient concentration of the active phosphorus the water had been boiled away till the solution was nearly concentrated with sodium carbonate. Since such a big quantity of sodium carbonate was found to disturb the digestion in later experiments another method was followed.

For that purpose the water was boiled away out of the solution of phosphoric- and sulphuric acid; the sulphuric acid was removed by fuming at a temperature as low as possible. The residue was received in water, filtrated and titrated with 0.2 n sodium hydroxide, indicator methyl red. The pH of this solution of sodium phosphate varied from six till seven (controlled with phenol red). In special experiments the yield of phosphorus obtained by this method was determined; it averaged about 60 per cent of the amount added to the sulphur. Now the determination of the radioactivity of the solution happens as follows. A fixed quantity of the solution was dropped on an aluminium foil, the water boiled away, after which the activity of the residue was measured in a compensation ionization chamber.

Determination of the radioactive phosphorus isotope.

With the ionization chamber mentioned above, the ionization current produced by the β-particles, emitted by the radioactive phosphorus in the preparation of the organs, was compared with the ionization current of a constant source, in this case the γ-activity of a piece of pitch blend [7]). Because the β-particles are partly absorbed in the preparation of the various organs, a correction ought to be done in the estimated activity. For it the absorption was specially investigated in the following way.

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[7]) G. J. Sizoo and C. P. Koene, Physica **3**, 1053 (1936).

A quantity of radioactive phosphorus was spread out on an aluminium foil, and then covered with a layer of the ash of the rat. Now the activity was measured for various thicknesses of the layer. The decrease of the activity with increasing thickness of the layer was found to be exponential, within the limits of the accuracy of the measurement. The absorption curve is given in fig. 2. The mass-absorption coefficient μ was found to be 11.5 $cm^2\ g^{-1}$. In our tests the labelled phosphorus was

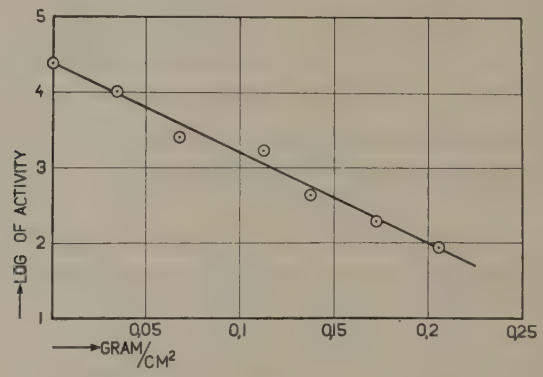

Fig. 2.

uniformely distributed through the material. Therefore to obtain the true activity of a preparation the measured activity must be multiplied with the factor $\frac{\mu d}{1 - e^{-\mu d}}$ in wich d means the thickness of the preparation, expressed in grams cm^{-2}. Mostly this correction was very small; only for the preparations of the residue the correction was rather large.

To check the correctness of the method a control test was made. A certain quantity of a solution of active sodium phosphate with an activity of 159 units was administered to a rat with a pipette. The pipette was rinsed with water, whereas the activity of this water was found to be 7.4 units. The rat was carbonized at 200 degrees centigrade. The total weight of the "ash" was 34 grams. A preparation of 134 mg/cm^2 of this ash showed an apparent activity of 16. The correction factor was calculated to be 1.93. Therefore the activity of the preparation was 31, whereas the total activity of the ash was calculated to be 151. This value is in excellent agreement with the activity of the administered solution.

Finally the activity of all preparations had to be corrected for the decay of the phosphorus. The half value period of the radioactive phosphorus was determined to be 15 days. In the physiological experiments all the activities were reduced to the time at which the activity of the solution was measured.

The administration of the labelled phosphorus.

The aqueous solution of sodium phosphate was administered in two different ways. For that purpose, in four experiments a fixed quantity

was inserted with an exactly calibrated pipette into the stomach of the rat through a small stomach tube. It was seen to no rest of the active solution remained behind in the tube or in the pipette. Moreover the tube and pipette were rinsed with water after every use, whereas the water was kept for testing. The rats used in these experiments starved 20—24 hours. This starvation facilitated the technique of inserting the tube into the stomach; furthermore, in the "treated" animals, it prevents, that an eventual action of vitamin D on the absorption of the phosphorus of the diet takes place before the active phosphorus was fed. In two experiments the active solution was injected into the tail vein after it had been made isotonic by adding sodium chloride. In these experiments, in which only normal and rachitic rats were used, no starvation was applied.

The making of the preparations of the different parts of the rats to be measured.

A certain time after the administration of the labelled phosphorus, in the discussed series after 1, 2, 8 and 8½ hours, the rats were decapitated, whereby as much blood as possible was caught in a tared cup. Then the rats were quickly sectioned. The oesophagus was ligatured near to the pro-stomach, whereas the ileum was doubly ligatured close to the caecum. Then the oesophagus was cut orally to the ligature, the ileum between the two ligatures; the stomach and small intestine were brought into a tared cup, whereas the same was done with the large intestine to which both the bladder and the faeces and urine produced after the administration of the phosphorus were added. The limb bones were then dissected, cleaned and brought into a tared cup. Finally the residue of the body with the head was collected.

Now the preparations were made as follows. The tared cups with the blood, the stomach, the small intestine, the large intestine, the bladder the faeces and urine were dried in an oven at 105 degrees centigrade for about 24 hours, after which the cups were weighed again. Then the dried matter of the mentioned organs and fluids was pulverized in a mortar, the powder sieved and suspended in ether, whereafter the suspension was poured out into a flatly grinded ring of glas, which was placed on a tared aluminium foil. The ring was pressed on the foil by loading it with a weight or an other object, to prevent that the ether flows away. Then the ether was evaporated at room temperature after which a flat layer of the dried organ with uniform thickness remained behind on the foil. Now the foil with the layer were weighed, the activity measured and corrected in the mentioned ways. The preparation of the blood measured was only a small part of the whole blood in the body of the rat. Therefore, the true activity for the whole blood must be calculated; this was done by the tables of DONALDSON [8]).

[8]) H. H. DONALDSON, The Rat. Memoirs of the Wistar Institute of Anat. and Biology, nr. 6 (1924).

As to the limb bones, in the first experiment, they were extracted with ether for 48 hours and then ashed at 500—600 degrees centigrade. By this method a part of the phosphorus was lost. For that reason a new procedure was followed. Herewith, the bones not being extracted, were carbonized in an oven at 200 degrees centigrade. Experimentally it was found that no phosphorus was lost in this procedure. Then the coal was pulverized, sieved and treated as was described for the blood and the viscera. Here it was necessary to add ½ g. of soluble starch to the preparation with the view to do it adhere to the foil. After correction of the estimated activity the true value was calculated for the whole skeleton by the tables of DONALDSON.

Finally the residue of the body in the first experiment was dissolved in hot sodium hydroxide by boiling for several hours; then, after being neutralized, the solution was dried and made into a preparation. However, the quantity of the dried matter was so large, that the preparation to be measured was about $^1/_{40}$ part of the whole residue. Of course in this way no exact results could be obtained. So, these figures for the first experiment were not calculated.

Therefore, in the further experiments for the residue the same procedure was used as had been described for the bones. Herewith it was also carbonized and then treated as the bone preparations. The activity reduced to the whole residue was diminished with the activy both for the blood and the part of the skeleton contained in it. Finally the mentioned corrections were made to obtain the true activity of the whole residue.

Discussion of the experiments.

The first experiment was made on 13 rats from which 4 were normals (N), 4 rachitic- (R), whereas 5 were "treated" animals (T). In accordance with the technique mentioned before an aqueous solution of the radioactive sodium phosphate was inserted into the stomach of the rats. The quantity of the administered solution ranged from 1.0 to 1.15 cm^3, containing about 1,25 mg. of the labelled phosphorus [9]).

One hour after the solution was administered the rats were killed, whereafter the preparations of the different parts of the rat were made. As was discussed before, in this experiment the percentage of the administered phosphorus in the residue was not calculated.

In the second experiment 12 rats were used. All had received about 2 mg. of the labelled phosphorus in an aqueous solution of sodium phosphate, which was inserted into the stomach. Two hours after the oral administration the rats were decapitated. In this experiment the activity of the residue was also determined. Since the gross absorption in the experiments mentioned before was too small, it was decided to decapitate

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[9]) A rough estimation of the content of the radioactive isotope $^{32}_{15}P$ leads to about 10^{-9} g. per mg. of the preparation.

TABLE 1.

Experiment and Group	Percentage of the administered P in dried matter of all the blood, the whole organs and excretions						Percentage of administered P in 100 mg. dried matter		
	Blood	Stomach and small intestine	Large intestine and faeces and urine	Skeleton	Residue after correction	Total	Blood	Skeleton	Residue after correction
Exp. I (Rats decapitated after 1 hour)									
N.	0.—	69.6	0.—	13.5		83.1	0.—	0.26	
N.	0.—	58.8	2.1	18.0		78.9	0.—	0.29	
N.	1.75	43.3	8.5	23.9		77.5	0.10	0.45	
N.	0.—	51.1	3.8	10.6		65.5	0.—	0.18	
R.	1.3	57.1	5.3	13.9		77.6	0.10	0.30	
R.	3.1	60.5	3.6	0.—		67.2	0.25	0.—	
R.	5.1	52.5	13.3	11.3		82.2	0.30	0.21	
R.	0.—	47.8	2.3	0.—		50.1	0.—	0.—	
T.	18.6	63.0	7.0	14.0		102.6	1.61	0.42	
T.	14.0	50.6	10.3	12.2		87.1	1.17	0.34	
T.	12.8	57.7	15.5	4.6		90.6	1.02	0.12	
T.	7.2	54.1	2.4	3.1		66.8	0.60	0.09	
T.	19.2	50.9	3.2	12.9		86.2	1.65	0.38	
Exp. II (Rats decapitated after 2 hours)									
N.	0.—	60.8	7.7	8.7	26.0	103.2	0.—	0.28	0.15
N.	23.1	52.0	9.0	8.0	13.0	105.0	1.82	0.20	0.06
N.	11.3	64.3	3.0	7.7	7.0	93.3	1.02	0.23	0.04
N.	9.0	22.4	6.1	6.5	53.5	97.5	0.75	0.19	0.28
N.	7.3	45.2	1.5	3.7	13.0	70.7	0.86	0.15	0.09
R.	2.8	69.5	0.—	3.3	23.9	99.5	0.32	0.13	0.17
R.	2.2	85.2	2.0	4.4	10.7	104.5	0.21	0.15	0.06
R.	15.5	49.5	2.5	4.8	23.5	95.8	1.52	0.17	0.14
T.	6.5	37.4	0.5	7.1	38.6	90.1	0.84	0.35	0 31
T.	1.8	67.2	0.2	8.6	18.2	96.—	0.18	0.32	0.11
T.	18.9	57.3	4.9	7.8	0.—	88.9	2.15	0.32	0.—
T.	2.8	25.9	8.4	15.2	50.4	102.7	0.25	0.46	0.27

TABLE 1. (*Continued*)

Experiment and Group	Percentage of the administered P in dried matter of all the blood, the whole organs and excretions						Percentage of administered P in 100 mg. dried matter		
	Blood	Stomach and small intestine	Large intestine and faeces and urine	Skeleton	Residue after correction	Total	Blood	Skeleton	Residue after correction
Exp: III (Rats decapitated after 8 hours)									
N.	12.6	15.4	30.3	16.3	25.1	99.7	0.90	0.35	0.10
N.	5.6	6.7	27.2	14.3	36.0	89.8	0.47	0.39	0 17
N.	16.0	4.1	49.1	10.0	20.4	99.6	1 66	0.38	0.13
R.	0.5	19.8	11.0	16.3	43.3	90.9	0.04	0.43	0.20
R.	9.4	8.2	14.2	17.4	48.5	97.7	0.75	0.46	0.22
R.	14.1	8.1	9.5	11.1	51.7	94.5	1.08	0.27	0.23
R.	13.9	19.7	13.8	15.2	42.8	105.4	0.93	0.30	0.16
T.	0.—	7.4	15.8	18.0	18.0	59.2	0.—	0.50	0.08
T.	9.7	18.0	7.6	13.7	44.8	93.8	0.91	0.44	0.25
T.	34.7	15.0	5.3	16.0	22.8	93.8	2.37	0.33	0.09
T.	24.7	15.8	11.4	15.7	33.2	100.8	2.20	0.48	0.18
Exp. IV (Rats decapitated after $8^1/_2$ hours)									
N.	12.0	12.0	10.6	22.0	42.6	99.2	1.17	0.83	0.26
N.	4.0	6.0	13.7	14.6	57.0	95.3	0.47	0.60	0.40
N.	27.9	11.1	37.8	4.2	18.1	99.1	3.50	0.17	0.14
R.	15.5	15.6	10.1	14.4	50.0	105.6	1.64	0.59	0.33
R.	10.3	10.2	9.1	12.6	52.9	95.1	1.09	0.51	0.33
R.	5.8	9.0	18.0	14.2	45.5	92.5	0.80	0.64	0.40
R.	0.6	15.5	20.3	15 9	54.9	107.2	0.07	0.65	0.42
R.	15.4	13.2	44.4	26.2	6.7	105.9	1.64	1.07	0.04
T.	2.9	9.2	15 8	20.4	56.7	105.0	0.31	0.83	0.37
T.	21.8	9.5	20.7	17.0	27.2	96.2	2.66	0.78	0.20
T.	4.0	12.3	14.6	13.9	41.7	86.5	0.50	0.64	0.30
T.	1.9	3.8	44.0	4.2	45.7	99.6	0.20	0.17	0.29

the rats about 8 hours after the oral administration of the phosphorus. This was done in the third experiment, which was carried out with 11 rats. The fourth experiment must be considered as a repetition of the preceding one; it was carried out with 12 rats, which were decapitated 8½ hours after the solution of sodium phosphate was inserted into the stomach.

The figures of these four experiments are reproduced in table 1.

In the fifth and sixth experiment an isotonic solution of sodium phosphate was injected in the tail vein, in order to eliminate the influence of the absorption. The figures of these experiments are tabulated in table 2.

TABLE 2.

Experiment and Group	Percentage of injected P in dried matter of all the blood, the whole organs and excretions						Percentage of injected P in 100 mg. dried matter		
	Blood	Stomach and small intestine	Large intestine and faeces and urine	Skeleton	Residue after correction	Total	Blood	Skeleton	Residue after correction
Exp. V (Rats decapitated after 1 hour)									
N.	0.—	12.9	6.4	24.1	49.4	92.9	0.—	0.40	0.14
N.	0.—	4.9	9.0	30.9	52.8	97.6	0.—	0.50	0.15
N.	6.1	7.3	2.6	22.3	56.5	94.8	0.32	0.36	0.17
N.	18.6	8.6	2.4	23.7	39.8	93.1	0.98	0.38	0.12
Exp. VI (Rats decapitated after 2 hours)									
N.	0.—	15.1	2.3	11.8	62.6	91.8	0.—	0.49	0.44
N.	8.1	10.5	4.1	32.7	50.1	105.5	1.00	1.35	0.36
N.	35.8	10.0	2.8	30.4	12.0	91.0	4.04	1.26	0.09
R.	18.2	0.—	1.3	57.7	14.2	91.4	2.14	2.35	0.10
R.	18.8	9.4	4.7	39.1	33.7	105.7	2.35	1.63	0.28
R.	45.2	22.4	0.—	4.8	22.5	94.9	6.00	0.20	0.19

Now considering the figures from the different experiments it is to note, that the distribution of the labelled phosphorus in the organism could be followed up easily. Except in a few cases, the whole of the quantity of the radioactive isotope administered could be recovered with a satisfactory accuracy. So our technique was reliable.

As far as the figures of the blood are concerned in the various experiments, herewith the variation is very large, both by oral administration and by injection of the active phosphorus.

In the experiments in which the phosphorus was injected into the tail vein the unexpected fact was observed, that within one hour in several rats the injected phosphorus had fully disappeared from the blood, but in other animals the blood contained a considerable part of the injected phosphorus. This fact proves, that the deposition of the active phosphorus of the blood into the different organs is regulated by factors, the action of which shows a large fluctuation by various animals. In this respect a characteristic difference between the normal, rachitic and "treated" animals could not be observed in these experiments.

Looking at the figures of the phosphorus distribution in the skeleton a very rapid entrance of the active phosphorus into the bone was perceptible.

If the amount of phosphorus deposed in 100 mg. of the dried matter of the skeleton was calculated for the percentage of the phosphorus inserted into the stomach, it was shown that 8 hours after the oral administration a somewhat larger quantity was deposed than after two hours. However, if these figures were reduced for the percentage of the absorbed phosphorus, it was evident that always about a constant percentage of the absorbed phosphorus was deposed in the skeleton. The percentage of the phosphorus deposed in the skeleton seemed also a constant part of all the active phosphorus deposed in the whole organism. Significant differences between the normal-, rachitic- and "treated" animals were not found.

As to the gross absorption, that is the difference between the quantity of phosphorus administered and the quantity present in the stomach and small intestine after a certain period, it may be established from table 3, that vitamin D did not act on the absorption. Although the figures for the different animals were divergent, at all events the gross absorption both in the normal and "treated" rats was not larger than in the rachitic animals. The same can be said about the re-excretion into the gut in the three groups of rats. It is to note that no value must be set on the averages, because the variation in the figures was too large. They were only calculated to give an impression into this value for the several groups. In the third series we thought we could see a difference in the deposition in the body of the three groups of animals. The total deposition, that is the gross absorption less the re-excretion, in normal rats averaged 55 %, whereas in rachitic and "treated" animals it averaged 75 %. However, in the fourth series we could not confirm these results.

A characteristic mode of action of vitamin D on the absorption of the active phosphorus from the gut or on the re-excretion into the gut could not be demonstrated in these experiments.

A very interesting observation was made in the experiments 5 and 6. As is shown by the figures in table 2, it is a fact that there is not only a very rapid absorption of phosphorus from the gut, but also a rapid excretion of the injected active phosphorus into the gut. One hour after

the injection into the tail vein, a considerable amount of the active phosphorus was re-excreted into the small intestine. This re-excretion can only happen with the digestion juices, after the labelled phosphorus was

TABLE 3.

Exper.	Gross absorption in percents of the phosphorus administered			Deposition in the whole organism in percents of the phosphorus administered		
	Normal	Rachitic	"Treated"	Normal	Rachitic	"Treated"
I	30.4	42.9	37.0	30.4	37.6	30.0
	41.2	39.5	49.4	39.1	35.9	39.1
	56.7	47.5	42.3	48.2	34.2	26.8
	48.9	52.2	45.9	45.1	49.9	43.5
			49.1			45 9
Average	44.3	45.5	44.7	40.7	39.4	37.1
II	39.2	30.5	62.6	31.5	30.5	62.1
	48.0	14.8	32.8	39.0	12.8	32.6
	35.7	50.5	42.7	32.7	48.0	37.8
	77.6		74.1	71.5		65.7
	54.8			53.3		
Average	53.5	32.3	53.0	48.0	30.7	47.0
III	84.6	80.2	92.6	54.3	69.2	76.8
	93.3	91.8	82.0	66.1	77.6	74.4
	95.9	91.9	85.0	46.8	82.4	79.7
		80.3	84.2		66.5	72.8
Average	91.3	86.1	85.9	55.7	73.9	75.9
IV	88.0	84.4	90.8	77.4	74.3	75.0
	94 0	89.8	90.5	80.3	80.7	69.8
	88.9	91.0	87.7	51.1	73.0	73.1
		84 5	96.2		64.2	52.2
		86.8			42.4	
Average	90.3	87.3	91.3	69.6	66.9	67.5

moved with the bloodstream and deposed into the several organs. A characteristic difference in these figures between the normal and rachitic rats could not be observed.

Summary and conclusions.

Experiments on phosphorus metabolism in normal, rachitic and "treated" rats with a radioactive phosphorus isotope as an indicator are reported. The preparation of the phosphorus isotope $^{32}_{15}P$ was described just as the determination of the radioactive phosphorus in the preparations of the several parts of the body.

The distribution of the phosphorus in the organism could be followed up easily; almost the whole of the quantity of the radioactive phosphorus administered could be recovered. Both by the administration with the stomach tube and by the injection into the tail vein a very rapid entrance of the labelled phosphorus in the bone was perceptible. Neither the increase of the gross absorption nor the increase of the total deposition of the active phosphorus in the whole organism, significantly raised the percentage of this phosphorus deposed in the skeleton. Furthermore it was observed, that one hour after the injection in the tail vein, a considerable amount of the active phosphorus was re-excreted into the small intestine; this can only happen with the digestion juices after the phosphorus was moved with the bloodstream and deposed into the several organs. So far as the gross absorption was concerned no difference could be observed in the period between 1 and 8 hours after the administration in the normal, rachitic and "treated" rats. The same can be said about the re-excretion into the gut. A characteristic mode of action of vitamin D on the absorption or re-excretion into the gut from the administered phosphorus could not be demonstrated.

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Experimental Morphology. — *Biologischer Nachweis zweier neuer Hormone durch Rhodeus amarus als Eichungsobject.* Von J. J. DUYVENÉ DE WIT. (Aus dem Labor. für experimentelle Morphologie des Zool. Institutes d. Univ. Utrecht; Leiter: G. C. HIRSCH). (Vorläufige Mitteilung). (Communicated by Prof. H. J. JORDAN).

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Injiziert man oestrogene Substanzen weiblichen Bitterlingen (Rhodeus amarus), so wächst die Legeröhre aus (FLEISCHMANN und KANN, 1932).

Seit 1935 habe ich diesen „Fischtest" ausgearbeitet zu einer Eichungsmethode, welche gestattet, die Menge der wirksamen Substanzen, welche sich in Drüsen, im Harn u.s.w. befinden können, mit einer Fehlerquelle von etwa 20 % zu messen. Der Einfluss der Jahreszeiten auf das Legeröhren-Wachstum kann durch einige Kunstgriffe ausgeschaltet werden.

Die Eichung, welche unter optimalen Verhältnissen stattfindet, beruht darauf, dass das Wachstum der Legeröhre, innerhalb einer bestimmten Zeit, proportional ist der Menge wirksamer Substanz. Also ist innerhalb bestimmter Grenzen das Legeröhren-Wachstum ein Maszstab für die Konzentration der wirksamen Substanz.

Mit Hilfe dieser Eichungsmethode wurde nun folgendes gefunden:

Die Verkettung der Hormone.

a. Nach Hinzufügung von wirksamen Schwangerenharn zum Wasser der Fische setzt das makroskopisch sichtbare und messbare Legeröhren-Wachstum erst nach 5½—6 Stunden ein; 12—14 Stunden nach der Verabreichung des Harnes biegt die Wachstumskurve, welche gradlinig verläuft ab: das Wachstum hört auf.

Die Dauer der anfänglichen Latenzzeit von 5½—6 Stunden ist zwar beeinflussbar durch die Temperatur; die Harnkonzentration dagegen übt hierauf keinen Einfluss aus.

b. Nach Hinzufügung von Follikelsaft aus Schweineovarien zum Wasser setzt dagegen das makroskopisch sichtbare Wachstum der Legeröhre schon nach einer Latenzzeit von 1—1½ Stunden ein; und 6—8 Stunden nach der Verabreichung des Follikelsaftes hört das gradlinige Wachstum auf.

Eine direkte Wirkung der wirksamen Harnsubstanz auf die Legeröhre ist darum ausgeschlossen, weil in diesem Falle die Anfangslänge der Legeröhre entscheidend sein müsste für die Längenzunahme in einer bestimmten Zeit und bei einer bestimmten Konzentration der wirksamen Substanz. Dies ist aber nicht der Fall; vielmehr ist die Längenzunahme innerhalb bestimmter Grenzen unabhängig von der Ausgangslänge der Legeröhre.

Aus dieser Tatsache und aus dem obengenannten Unterschiede in der Latenzzeit habe ich die Hypothese gewonnen, dass die aktive Substanz des Schwangerenharns irgend eine Drüse reizt, welche ihrerseits eine, mit dem wirksamen Stoff aus Follikelsaft identische Substanz absondert, welche das eigentliche Wachstum der Legeröhre zur Folge hat. Später zu publizierende histologische Untersuchungen und Versuche mit fraktionierter Harnverabreichung, welche direkte Schlüsse zu ziehen gestatten, sprechen dafür, dass das Ovar die Drüse ist, welche teilweise von der Harnsubstanz transformiert wird und daraufhin das Wachstumshormon sezerniert, wodurch die Verlängerung der Legeröhre zu stande kommt. Es scheint also folgende *Kettenreaktion* vorzuliegen: Eine gonadotrope Harnsubstanz → Transformation des Ovars → Sekretion eines oestrogenen Hormons → Wachstum der Legeröhre.

Biologische Analyse der beiden Hormone.

a. Nach Verabreichung der 100-fachen Menge Oestron, welche maximal in der verwendeten Menge Harn vorhanden sein könnte, tritt erst spät ein Wachstum der Legeröhre ein. Die entsprechende Menge gonadotroper Substanz zeigte keine Einwirkung. Kochen des Harns zerstört die aktive Substanz nicht, im Gegensatz zu den bisher bekannten gonadotropen Hormonen. Die Substanz kann im Gegensatz zu Oestron aus nativem Harn ohneweiteres nicht mit Aether extrahiert werden. Die im Harn wirksame Substanz kann also weder Prolan noch Oestron sein. Nach ihrer Wirkung scheint die unbekannte Substanz eine gonadotrope zu sein, weil sie offenbar auf das Ovarium einwirkt; dies wird die folgende histologische Untersuchung auch zeigen. In der weiteren Diskussion möchten ich diese, meines Wissens niemals genauer biologisch definierte, gonadotrope *Substanz aus dem Harn, Lutidin* nennen. (EHRHARDT und KUEHN haben bereits 1933 auf das wahrscheinliche Vorkommen eines oestrogenen „Legeröhrenhormons" hingewiesen, ohne exaktere Beweise zu geben für die Unterschiede dieses Hormons gegenüber Oestron.)

b. Nach Verabreichung der 1000-fachen Menge Oestradiol, welche in der verwendeten Menge Follikelsaft vorhanden sein kann, tritt erst nach längerer Zeit ein unerhebliches Wachstum der Legeröhre ein. Die wirksame Substanz aus dem Follikelsaft kann also kein Oestradiol sein.

Ihrer Wirkung nach scheint diese unbekannte Substanz des Follikelsaftes, welche kochbeständig ist, und leicht mit Aether extrahiert werden kann, eine oestrogene zu sein. Einfachkeitshalber möchte ich diese, meines Wissens noch nicht biologisch definierte *Substanz aus Follikelsaft* in der weiteren Diskussion *Oviductin* nennen.

Zeigen nun andere Körpersubstanzen auch diese direkte oder indirekte positive Einwirkung auf die Legeröhre?

a. Wässrige Extrakte von Schweine-Ovaria und Corpora lutea,

menschliche Plazentae, Bullen- und Widder-Testes und Rinder-Nebennieren, erwiesen sich als wirksam im Fischtest.

b. Wässrige Extrakte aus Thyreoidea, Pankreas, Cerebrum, Hypophyse, Epiphyse, Thymus, Milz, Leber und Dünndarm waren völlig unwirksam.

Androsteron und Testosteron in relativ hohen Dosen zeigten, wie Oestron und Oestradiol, nur eine schwache Wirkung, welche etwa nach einer Stunde evident wurde. Das Lutidin ist also kein männliches Hormon.

Ob die wirksamen Substanzen aus diesen genannten Körperteilen identisch sind mit Lutidin oder Oviductin muss noch untersucht werden.

Physiologische Ergebnisse.

a. Bei einer Reihe schwangerer Frauen wurde die Lutidin-Konzentration im Harn untersucht. Es zeigte sich, dass die Konzentration dieses Hormons im Harn von dem 2. bis 10. Schwangerschaftsmonat konstant bleibt, also ganz im Gegensatz zu dem, was bei Oestron und Prolan der Fall ist, wo ein erheblicher Anstieg während der Schwangerschaft beobachtet wird.

b. Bei einer Reihe normal menstruierender Frauen wurde die Lutidin-Konzentration im Harn untersucht. Es zeigte sich, dass die Konzentration während der Menstruation abnimmt; dann folgt ein geringer Anstieg, welcher während der Ovulation fast wieder verschwunden ist. Der grösste Anstieg erfolgt am 19. bis 26. Tage post menstruationem. Die hier erreichte Konzentration stimmt überein mit derjenigen, welche während der Schwangerschaft gefunden wird, also im Gegensatz zu Oestron und Prolan, wo die maximalen Ausscheidungen während des Cyclus viel geringer sind als während der Schwangerschaft. Die Lutidin-Konzentration im Harn kann also nicht als Kriterium für eine etwaige Schwangerschaft gelten.

c. Solange der Mann potent ist, befindet sich Lutidin oft in seinem Harn und zwar in etwas niedrigerer Konzentration wie bei schwangeren Frauen.

d. Harn trächtiger Stuten und Kühe ist nur wenig bezw. kaum wirksam.

e. Im Harn eines krebskranken Mannes und einer krebskranken Frau wurde keine abnormale Konzentration von wirksamer Substanz gefunden.

f. Bei zwei Fällen von Mola hydatidosa wurde keine erhöhte Lutidinkonzentration im Harn gefunden.

Wenn ich mich nicht täusche, bieten obenstehende Befunde für die Zukunft folgende Perspektive : Bisher wird dasjenige, was wir von der Endokrinologie wissen grösstenteils ermittelt durch die allgemein verwendeten Testobjekte wie Nagetiere und Hühner. Sehr wahrscheinlich gibt es beim Menschen aber endokrinologische Phänomene, welche mittels dieser Tiere nicht erfasst werden können. Verwendet man dagegen Testobjekte, welche aus ganz anderen Tiergruppen stammen, so ergibt sich vielleicht die Mög-

lichkeit, die von Nagetieren und Hühnern nicht zu erfassenden Phänomene nachzuweisen, bzw. zu studieren. Das scheint sich nach meinen Erfahrungen am Bitterling tatsächlich zu bewähren und es scheint nicht ausgeschlossen, dass mittels Rhodeus amarus als Testobjekt ein neues Gebiet in der Endokrinologie zugänglich gemacht werden kann.

Diese Arbeit wird jetzt im Labor. für exper. Morphologie in drei Richtungen weitergeführt:

1. Die Cytologie und Histologie von Rhodeus amarus vor und nach Verabreichung von wirksamen Substanzen wird bearbeitet.
2. Es wird versucht, die Lutidin- und Oviductin-Extrakte zu reinigen und zu isolieren.
3. Es werden auch Eichungen an Harn und Blut vorgenommen von Patienten mit (poly)hormonalen Störungen.

Die ausführliche Darstellung der Ergebnisse erscheint in Kürze in meiner Doktorarbeit, wo ich auch allen denen meinen Dank aussprechen werde, die mir so reich geholfen haben.

FLEISCHMANN und KANN, Pflüg. Arch. Bd. **230**, 1932, S. 662.
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